STUDIES RELATED TO CATIONIC POLYMERISATION

by

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A Thesis submitted to the UNIVERSITY of KEELE in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

December, 1964.

"polymer letters" between

p.161 +162

"proc.chem.soc.1964" between

p.140 +141

"proc.chem.soc.1964" between

p.56 +57

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ACKNOWLEDGMENTS

I wish to thank Professor H. D. Springall, for providing the facilities to carry out the present work.

To Dr. P. H. Plesch, who suggested this work, keenly supervised its progress, criticised constructively my way of approaching its general problems, and made my stay at Keele such a pleasant and exciting one, I wish to express my deepest gratitude.

Miss V. Roe has helped me most adequately in the experimental routine work; for this I thank her sincerely.

Also, I wish to acknowledge the helpful criticisms and discussions with the members of Dr. Plesch's polymer group.

Finally, I thank the United States Rubber Company for a generous two-years grant.

ABSTRACT

The work described in this Thesis is concerned with the identification of the chain carriers in polymerisation systems involving acid and Lewis-acid catalysts.

In a preliminary study of the spectroscopic and conductimetric properties of carbonium ions derived from carbinols and olefins it was found that the phenylethanols are dehydrated by strong mineral acids to the corresponding olefins before protonation takes place (Chapter Two).

The protonation of triphenylethylene gives a classical carbonium ion which can react with excess of olefin to produce a radical ion (Chapter Three).

The protonation of tetraphenylethylene gives a highly conjugated carbonium ion in which the proton is attached to one of the phenyl groups and not to the ethylenic double bond (Chapter Three).

The kinetics of the protonation of styrene by excess anhydrous perchloric acid and the spectroscopic properties of the 1-phenylethyl carbonium ion obtained in this reaction have been studied (Chapter Four).

Styrene is polymerised by perchloric acid and other acidic catalysts without formation of carbonium ions, and it has been shown that, in the case of $HClO_4$, the intermediate responsible for the polymerisation is the 1-phenylethyl perchlorate ester. The polymerisation kinetics have been investigated and the results agree with those of other

authors where they overlap. Other monomers, acenaphthylene and N-vinylcarbazole, behave similarly to s tyrene (Chapter Four).

These ester-catalysed polymerisations have been called pseudocationic. The pseudocationic polymerisation of styrene by perchloric acid is followed by formation of styryl ions, a complicated reaction which has been studied in some detail.

True cationic polymerisation has also been observed during this work, and it was found that carbonium ions are very powerful chain carriers giving reaction rates at least 100 times greater than the corresponding esters (Chapter Four).

In the course of this work the spectra of many carbonium ions have been fully characterised.

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INTRODUCTION

In spite of the vast amount of research which has been devoted to the problems related to cationic polymerisation during the last twenty years or so, many fundamental questions have remained almost completely unanswered. In particular, the very nature of the chain carriers present in a polymerising system has never been fully elucidated; whether these are free ions, ion pairs, or both, or yet some other species, is not known with certainty for most systems.

The most common approach to this basic problem has generally consisted in formulating a chemical interpretation of results obtained from kinetic and molecular weight measurements and from determinations of polymer structure. No direct method of identifying the chemical nature of the chain carriers, applicable during the polymerisation, has yet been elaborated. It follows that not only can one say very little about the chemistry of the chain carriers, but that the other fundamental aspect of this problem, namely the determination of their actual concentration at any given time during the polymerisation has not yet found a solution. This has generally precluded the possibility of calculating fully reliable values for the rate constant of propagation, k_p, from the experimental results. There may be a few exceptions to this negative situation and they will be analysed in detail later in this thesis.

Ever since Whitmore[1] first gave his interpretation of the chemistry of acid-catalysed polymerisations of olefins, based on a carbonium ion mechanism, the whole body of work produced in this field has been focused around this basic postulate. It is impossible to cite typical references in order to illustrate this, for it is almost impossible[*] to find any work in which this interpretation is contested. It is therefore best to refer globally to Plesch's recent book[2] in which most of what has been written about cationic polymerisation is reviewed, commented upon and re-illustrated. Of considerable interest are also two recently published reviews on the subject, by Pepper[3] and Kennedy[4], respectively.

Given the generally accepted carbonium ion theory, it was obvious that with the advent of more refined techniques and instrumentations, researchers in cationic polymerisation should apply themselves to the identification, the characterisation, and the study of the behaviour of protonated species, in particular protonated monomers.

The most suitable techniques for the study of these entities are ultra-violet and visible spectroscopy, electrical conductivity and nuclear magnetic resonance spectroscopy.

U.v. and visible spectroscopy are best applied to aromatic and conjugated aliphatic compounds which give rise to carbonium ions absorbing from 275 mμ for the dimethylcyclopentenyl positive ion[5] up to

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[*] A detailed account of Whitmore's interpretation and of the few works in which this was contested, will be given in Chapter Four.

800 - 900 mμ for highly conjugated aromatic carbonium ions (see for example spectrum no. 8 , Chapter Three, this Thesis). The position of the absorbtion maxima of aliphatic carbonium ions is still very uncertain and it seems likely to lie at wave lengths lower than 270 mμ, the only ion in the class spectroscopically identified with certainty being the tricyclopropylmethyl cation[6] with λ_{max} at 270 mμ.

A large number of carbonium ions have been characterised spectroscopically but even in this apparently simple field there are unresolved obscurities (see Chapter Four). Several techniques can be adopted to produce stable ions, the most popular being the dissolution of a carbinol or olefin in a strong acid such as sulphuric acid;[7] others include the preparation of carbonium salts such as trityl perchlorate[8] and the use of acid clays which act as hydride extractors on paraffins, and as proton donors to olefins.[9] Aromatic carbonium ions produce peaks with extinction coefficients at maximum wave lengths ranging between 10^3 and 10^5, according to their structure. In particular, styrene dissolved in concentrated sulphuric acid has been reported to give rise to a visible peak at 430 mμ with $\varepsilon_{430} = 1000$ by Jordan and Treloar[10] and at 435 mμ with $\varepsilon_{435} \simeq 10{,}000$ by Grace and Symons;[11] in both works this peak is attributed to the 1-phenyl ethyl carbonium ion; it will be shown below (Chapter Four) that the values of ε are incorrect.

Conductivity measurements on carbonium ion solutions do not provide any way of characterising chemically the species present in

the system, but they can

a) lead to the computation of the relative population of free ions and ion pairs, and

b) reveal the presence of aliphatic carbonium ions in a more convincing way than spectroscopy does.

It has been shown[12,13] that for a given solvent the spectra due to free ions and ion pairs are identical; point a) is therefore essential to the study of these two species which are thought to play independent roles in some cationic systems.[14]

The use of N.M.R. spectroscopy, introduced only a few years ago, represents a most useful advance in the study of stable carbonium ions; many structural problems can be best solved by this technique.[6] It is my intention to continue in the near future some of the work recounted in this thesis and it is likely that N.M.R. spectroscopy will help to shed some light on various obscure points.

The working programme put forward at the beginning of this research was based on the following considerations: In order to approach the problems enumerated above in the most convenient and fruitful way, it is essential to start by studying species which do not polymerise when mixed with protonating agents, and to investigate their physico-chemical behaviour under conditions strictly similar to those of a polymerising system. These species should resemble closely in their chemical structure the currently used monomers. It could be expected that a system of this nature would

produce preliminary information on the initiation step and on the characteristics of the species which might be chain carriers in analogous polymerisation systems.

After this first stage, one could switch attention onto a polymerisable olefin, investigate the properties of its carbonium ions in isolation under suitable conditions, and then study the actual polymerisation.

From these and the earlier general considerations, it was decided that by far the most convenient catalyst-monomer pair would be perchloric acid-styrene. The polymerisation of styrene catalysed by anhydrous perchloric acid in 1,2-dichloroethane and other solvents has been thoroughly studied by Pepper and Reilly.[15] Reactions were followed dilatometrically in semi-open devices (water was shown to have little or no effect on the kinetic behaviour of the system up to $[H_2O] \simeq 20[HClO_4]$) and were found to be kinetically very simple. The reaction scheme put forward by the authors on the basis of their experimental results was as follows:

Initiation

$$CH_2{:}CHPh + HClO_4 \xrightarrow{k_i} CH_3.\overset{+}{C}HPh\ ClO_4^- \qquad R_i = k_i[P_1][HClO_4], \text{ fast}$$

(complete in a few seconds)

Propagation

$$CH_3.\overset{+}{C}HPhClO_4^- + CH_2{:}CHPh \xrightarrow{k_p} CH_3.CHPh.CH_2.\overset{+}{C}HPhClO_4^-$$

$$R_p = k_p[P_1][P_n^+]$$

. . . . . .

Spontaneous transfer

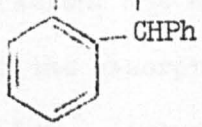
$$CH_3.CHPh.[CH_2.CHPh]_n.CH_2\ \overset{+}{C}HPhClO_4^- \xrightarrow{k_t} CH_3.CHPh.[CH_2.CHPh]_n.CH{:}CHPh + HClO_4$$

$$R_t = k_t[P_n^+]$$

Monomer transfer

$$CH_3.CHPh.[CH_2.CHPh]_n.CH_2.\overset{+}{C}HPhClO_4^- + CH_2{:}CHPh \xrightarrow{k_{tm}}$$

$$\rightarrow CH_3.CHPh.[CH_2.CHPh]_n.CH_2.CH - CH_2 + HClO_4$$



$$R_{tm} = k_{tm}[P_1][P_n^+]$$

$[P_1]$ = styrene concentration

$[P_n^+]$ = carbonium ion concentration

No termination could be detected, as shown by the fact that addition of a second quantity of monomer to the polymerised solution produced a polymerisation with a rate constant equal to the original one.

It was concluded from kinetic considerations that all the perchloric acid present in a given run would take part in the reaction and protonate an equivalent amount of styrene. The time-conversion curves were in fact strictly first order overall, and the rates were directly proportional to the acid concentration over a wide range of concentrations. The authors therefore produced values for the rate constant of propagation, k_p, at different temperatures and in different solvent mixtures, by simply measuring the slopes of the straight lines obtained by plotting the first order rate constant values obtained from the kinetic analysis of the time-conversion curves, against the corresponding acid concentrations.

The visible spectra of the polymerising systems, or rather of the polymerised systems, were studied at fixed initial monomer and variable catalyst concentration; the authors calculated the value of the extinction coefficient for the absorption maximum of the peak produced by the styryl (polystyryl) ion . Assuming that the ionic concentration would be equal to the acid concentration, they found ε to be about 160 at 416 mμ; the striking difference between this value and that of Jordan and Treloar (see page 3 , this Thesis) was attributed to the difference in solvents used.

Our choice of this system was dictated by two different kinds of considerations, namely:

a) Many obscure points seemed to persist in what appeared to be such a simple system. These were mainly: i) The apparent

incompatibility between the carbonium ion interpretation and the negligible effect of relatively large quantities of water on the polymerisation features; ii) the figures for the k_p's which seemed much too low, and the activation energies, which seemed toohigh for a carbonium ion propagation; iii) the very low value of the extinction coefficient for the absorption maximum of what was alleged to be the styryl ion. These "negative" reasons made the system appear worthy of further study.

b) Several "positive" features could be spotted, which appeared to be extremely important for our specific purposes. Amongst them were the absence of termination and the alleged high carbonium ion population; it was thought that these two factors might facilitate considerably the study of the total ionic concentration and the computation of the relative abundance of free ions and ion pairs. It was in fact thought, on the grounds of considerations recently published by Plesch,[14] that although the authors had postulated a mechanism involving only ion-pairs, the system would contain also free ions.

An additional stimulating reason for choosing this system was the fact that one could employ non-polymerisable olefins, similar in structure to the monomer, such as triphenyl- and tetraphenylethylene, to investigate some of the physico-chemical properties of the ionic species involved, in a less complicated context.

The main object of this work was therefore an approach to the fundamental problems discussed earlier, through a relatively simple

system, some of the features of which were already known. In view of the high sensitivity towards water normally displayed by carbonium ions, it was thought essential to work under strictly anhydrous conditions and therefore to use high vacuum techniques.

I set out in the traditional frame of mind, looking for ions on the assumption that they (paired or free) were the chain carriers in cationic polymerisation; I was forced to abandon the traditional view by the direct evidence of my results and observations.

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CHAPTER ONE

EXPERIMENTAL

PART I: MATERIALS

1. Solvents.

1.1 Methylene dichloride.

Commercial methylene dichloride supplied by I.C.I. Ltd. was purified as described by Weissberger,[1] and dried for one day over freshly ground calcium chloride in the dark. It was then fractionally distilled through a 4 ft. nickel turnings column at a reflux ratio of 5:1. Approximately 60% of the starting material was collected in dark bottles as middle fraction, b.p. 40.0°/754 mm (lit.[1] 40.1°/760 mm). A vapour phase chromatogram of this fraction showed the presence of traces of chloroform (about 1:10,000 vol/vol); no other impurities could be detected. In view of the fact that chloroform is by no means "poisonous" towards carbonium ions and that it was present in such small quantities, it was decided that this batch would be suitable for use without further purification. The solvent was then shaken with phosphorus pentoxide (B.D.H.) and quickly transferred into the vacuum-line reservoir (Fig. 1). After a thorough degassing and refluxing under magnetic stirring for several hours, the solvent was ready for use.

A few millilitres were vacuum distilled into a small glass tube

containing ground calcium hydride: no gas evolution could be noticed, a proof that the solvent was well dried.

A test was then carried out to check upon the possibility of phosphorus pentoxide being distilled over with the solvent. No residue was left on the bottom of a small flask when approximately 150 ml of the distilled solvent were evaporated to dryness; the flask walls were then rinsed with a few drops of distilled water but no acidity could be detected by a test paper.

Other properties of methylene dichloride, such as electrical conductivity, optical transparence, etc. will be discussed in the appropriate sections of this thesis.

Four batches of this solvent were used throughout this work and gave perfectly reproducible results. The solvent used for work in open systems was subjected to the same purification and stored in dark bottles over calcium chloride. Note: Silica gel for chromatographic use (B.D.H.) activated at 200° for several hours under vacuum was tried as drying agent for methylene dichloride and found to be ineffective. A portion of solvent vacuum-distilled from silica gel onto calcium hydride produced a vigorous evolution of hydrogen.

1.2 1,2-dichloroethane.

The commerical product, supplied by M. and B. Ltd., was shaken with a dilute solution of potassium hydroxide, then three times with distilled water. After prolonged standing over freshly ground calcium

chloride, the solvent was refluxed with calcium hydride for a few hours, then fractionated in a way similar to that used for methylene dichloride. About 70% of the initial amount was collected as middle fraction, b.p. 83.3°/755 mm (lit.[1] 83.4°/760 mm). A vapour phase chromatogram of this portion showed a single clean peak.

In order to ascertain that no reaction had taken place between the solvent and the drying agent, we compaired the v.p.c.'s of: i) the solvent before treatment with calcium hydride; ii) the solvent after refluxing with calcium hydride; iii) the head fraction from the fractionation. The chromatograms of all three were identical.

The solvent was then stored under its own vapour pressure in a reservoir attached to the main vacuum line (Fig. 1) over freshly ground calcium hydride. It was used after several days' degassing and refluxing when no more hydrogen was evolved. One batch of this solvent was used.

1.3 Nitromethane and Nitroethane.

Both these solvents (B.D.H., purity not less than 95%) were treated in the same way. They were refluxed with sodium bisulphite for two hours to remove aldehydes, then fractionally distilled at atmospheric pressure on a 2 ft. vigreux column with a reflux ratio of 10:1. The physical properties of the middle fractions (approximately 50% of the initial quantity) are shown in the Table below.

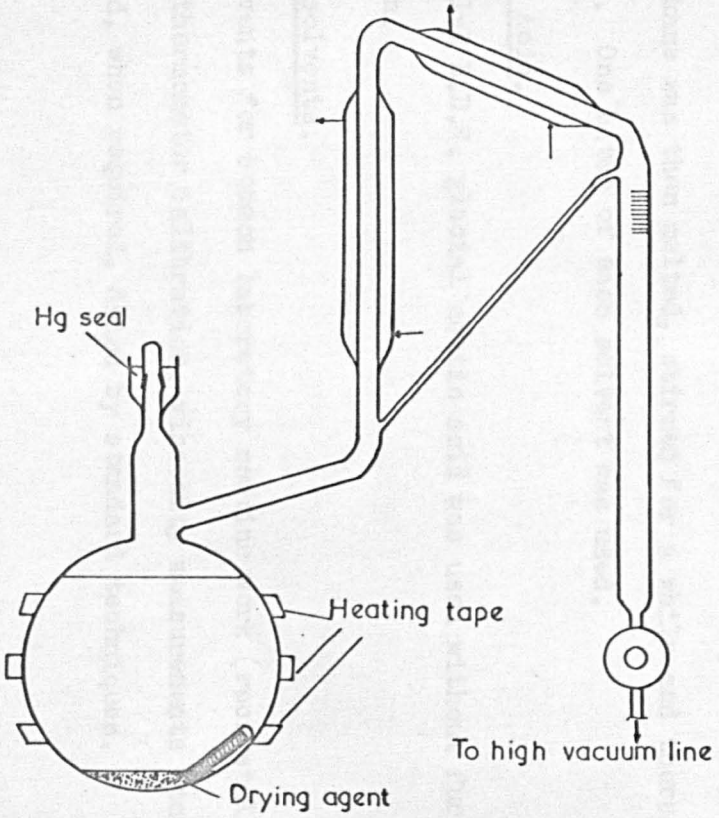


Fig.1 The storage and metering of chloroalkanes

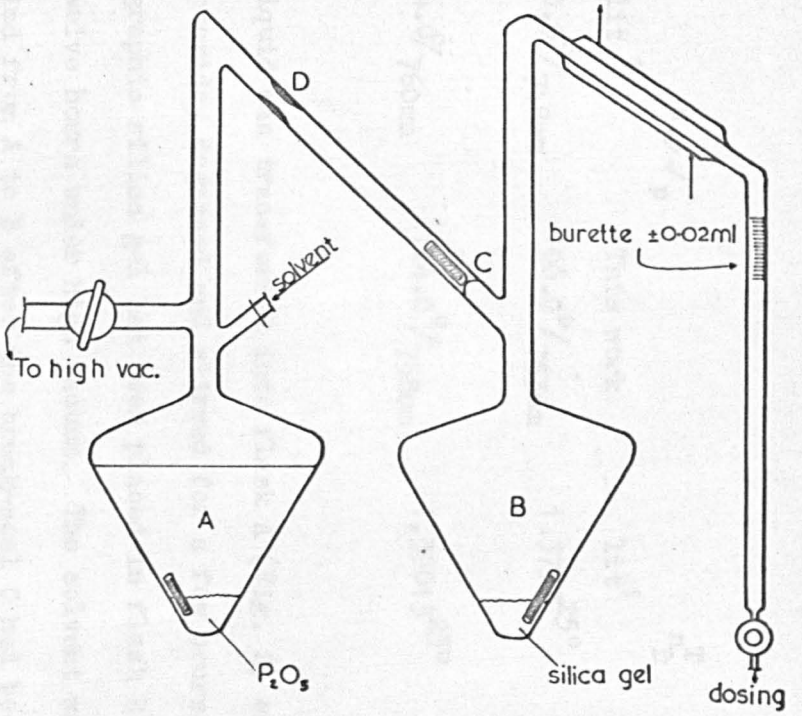


Fig.2 The drying and storage of the nitroalkanes

	b.p./$_p$		n_D^T	
	lit.[1]	This work	lit[1]	This work
CH_3NO_2	$100.5^\circ/_{748mm}$	$100.0^\circ/_{753mm}$	1.3797^{25°	1.3789^{26°
$C_2H_5NO_2$	$114.0^\circ/_{760mm}$	$114.0^\circ/_{758mm}$	1.39015^{25°	1.3903^{25°

The liquid was transferred into flask A (Fig. 2) containing phosphorus pentoxide, degassed and stirred for a few hours. Previously some chromatographic silica gel had been placed in flask B and activated at 300° for twelve hours under high vacuum. The solvent was then vacuum-distilled from A to B after the break-seal C had been cracked. At the end of the distillation flask A was removed by sealing off at D, the nitroalkane was then melted, stirred for a while and thereafter stored in the dark. One batch of each solvent was used.

1.4 Acetic Acid.

AnalaR B.D.H. glacial acetic acid was used without further purification.

1.5 Other solvents.

Solvents for common laboratory routine work (recrystallization, synthesis, thermometer calibration, viscosity measurements etc.) were purified and, when required, dried by standard techniques.

2. Olefins.

2.1 Styrene.

The commercial product (B.D.H. or Lights) was shaken with a concentrated NaOH solution to remove the inhibitor, washed three times with water, and then left standing overnight over barium oxide. It was then fractionally distilled under reduced pressure; the middle fraction, collected over CaH_2, was approximately 60% of the starting volume, b.p. $40^{\circ}/15$mm (lit.[2] $40^{\circ}/_{15.2mm}$). The olefin was then quickly transferred to flask A on the vacuum line (Fig. 3). This was sealed in E, the styrene thoroughly degassed by repeated thawing and freezing and stirred for a while with the calcium hydride. The break-seal C was then crushed and the styrene vacuum distilled to flask B where some BaO had been previously activated by prolonged heating at 360° under high vacuum. After flask A had been sealed off at D, the styrene was thawed; stirred with the drying agent and it was then ready for use.

Small quantities of monomer (2×10^{-3} - 0.5 mMoles) where dosed by placing a bath at known temperature around B (Fig. 3), opening the metal valve H and filling the empty volume F (approx. 1 litre) with styrene vapour. After a few minutes for equilibration, H was closed, J opened and the styrene transferred to the reaction device by cooling this with liquid nitrogen. Larger quantities (0.5-50 mMoles) were dosed to the reaction device or to breakable phials by vacuum distillation from the microburette G (accuracy $\pm$ 0.003 ml).

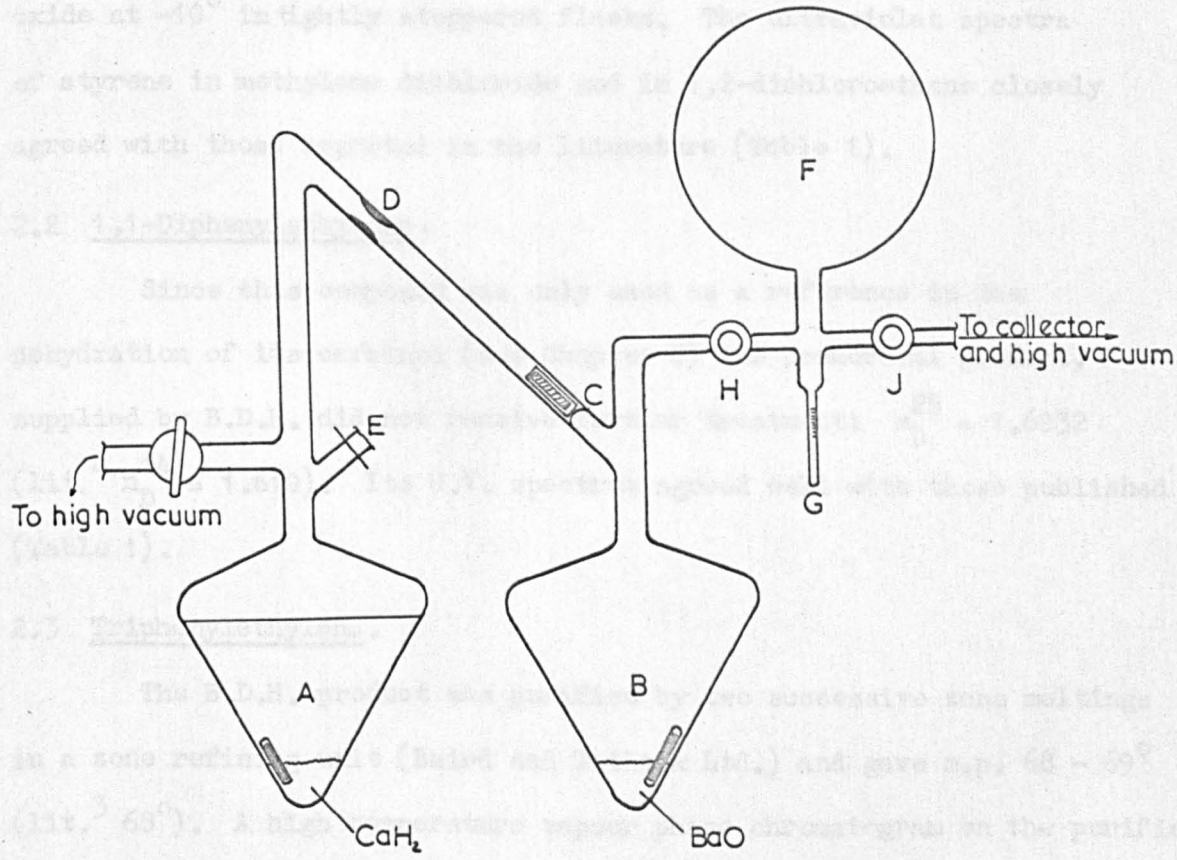


Fig.3 The drying and the dosing of styrene

The styrene was stored at liquid nitrogen temperature in the dark and did not show appreciable polymerisation after several weeks.

Four batches of this olefin were used throughout this work and gave identical results.

The styrene used for exploratory runs in open systems was subjected to the same purification treatment and stored over barium oxide at -10° in tightly stoppered flasks. The ultraviolet spectra of styrene in methylene dichloride and in 1,2-dichloroethane closely agreed with those reported in the literature (Table 1).

2.2 1,1-Diphenylethylene.

Since this compound was only used as a reference in the dehydration of its carbinol (see Chapter 2) the commercial product, supplied by B.D.H. did not receive further treatment; $n_D^{25} = 1.6032$ (lit.[4] $n_D^{14} = 1.610$). Its U.V. spectrum agreed well with those published (Table 1).

2.3 Triphenylethylene.

The B.D.H. product was purified by two successive zone meltings in a zone refining unit (Baird and Tatlock Ltd.) and gave m.p. 68 - 69° (lit.[3] 68°). A high temperature vapour phase chromatogram on the purified olefin in benzene solution, gave a single sharp peak.

Data on the U.V. spectra of its solutions in methylene dichloride and in acetic acid are given in Table 1.

2.4 Tetraphenylethylene.

Two different batches of this compound were used (Aldrich Ltd. and Kodak Ltd.) and gave identical results. The commercial product was recrystallised from 1,4-dioxane, washed with ethanol and thoroughly dried under high vacuum; m.p. 227° (lit.[4] 227°).

The U.V. spectrum in methylene dichloride closely resembled those previously published (Table 1).

2.5 Acenaphthylene.

The B.D.H. product was recrystallised twice from hexane; m.p. 93° (lit.[3] 92 - 93°). The U.V. spectrum of this compound agreed with those published (Table 1). The visible spectrum (spectrum 1) showed a peak at 465 mμ (ε = 25.1), not reported previously in the literature. Three different batches of purified acenaphthylene gave the same visible spectrum. It is likely that this unreported peak escaped other investigators because of its very low ε_{max}.

2.6 Acenaphthylene dimer.

This olefin was available in our laboratories, it having been prepared by Mrs. M. Panton. Data on its U.V. and visible spectrum are given in Table 1.

2.7 N-Vinylcarbazole.

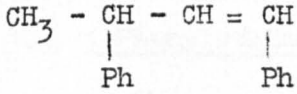
The commercial product from Lights was recrystallised from hexane and gave m.p. 96° (lit.[2] 97°). Its U.V. spectrum is reported (Table 1).

2.8 *α*-Methylstyrene.

The commercial product (B.D.H.) was fractionated under high vacuum, generous head and tail fractions being discarded. It was then kept under its own vapour pressure in a small flask attached to the vacuum line through a lightly greased tap. Dosings were performed using the same procedure as for styrene. Spectral data on this compound are given in Table 1.

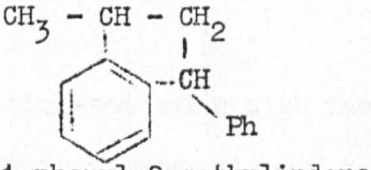
2.9 Styrene dimers.

Although the cyclic dimers of styrene are not olefins, the preparation of both the linear and the cyclic dimers is reported here for the sake of consistency. The procedure adopted by Risi and Gauvin[5] was followed. The reaction product was extracted with ether and the ether distilled off at atmospheric pressure. The thick oily liquid obtained was analysed in a high temperature v.p.c: the ratio of linear to cyclic dimers (these being mixtures of cis and trans-isomers) was about 4:1. A fractional distillation under reduced pressure of this mixture yielded as last fraction about 5 ml of pure linear dimer I, b.p. 172°/14mm (lit.[6] 163°/9mm and 181°/20mm), n_D^{25} = 1.5902 (lit.[6] n_D^{20} = 1.5932). Its v.p.c. showed that the cyclic content of this fraction was less than 0.1 %.



1,3-diphenylbutene-1

I



1-phenyl-2-methylindane

II

The rest of the distillate was refluxed with ten times its volume of 65% sulphuric acid for 40 hours in an attempt to increase its cyclic dimer content.[6] The reaction product was isolated and fractionally distilled: The first fraction (about 2 ml) collected at 163-164°/14mm contained approximately 97% of cyclic dimers II, and 3% of linear dimers. In view of the fact that the main concern were the linear dimers, I refrained from a further purification of the cyclic dimer. It was however, possible to obtain a spectrum of the pure mixture of cis- and trans-cyclic dimers dissolved in methylene dichloride by treating the solution of our product in CH_2Cl_2 with a small quantity of perchloric acid; the cyclization of the traces of linear dimer was complete in a few minutes.[7] Spectral data on I and II are given in Table 1. The I.R. spectra of I and II agreed well with those published.[6]

3. Carbinols.

3.1 Triphenylmethylcarbinol.

The commercial product from B.D.H. appeared to be of good purity and

was therefore used as obtained; m.p. 163° (lit.[3] 163°).

3.2 1-Phenylethanol.

This compound (B.D.H.) was fractionated under high vacuum and thereafter stored under its own vapour pressure at room temperature and dosed in the same way as styrene; $n_D^{25} = 1.5328$ (lit.[4] $n_D^{20} = 1.5395$):

3.3 1,1-diphenylethanol

The commercial product (Kodak) was used without further purification; m.p. 81° (lit.[3] 81°).

3.4 1,1,2-Triphenylethanol.

This compound was synthesised following Carter and Hay's procedure,[8] based on reactions I and II. The crystals obtained were recrystallised twice from light petroleum. After prolonged vacuum drying they melted at 91° (lit.[8] 88-90°).

$$PhCH_2Cl + Mg \rightarrow PhCH_2MgCl \qquad I$$

$$PhCH_2MgCl + PhCOPh \xrightarrow{H_2O} PhCH_2.CPh_2OH + MgClOH \qquad II$$

3.5 1,1,2,2-Tetraphenylethanol.

The photosynthesis of this compound was performed according to Banchetti's instructions[9] (reaction III). The crystals of carbinol were isolated, washed with petroleum ether, recrystallised once from cyclohexanol and once from CH_2Cl_2. White needles in rather low yield, melting at 239 - 240° (lit.[10] 238 - 239°), were obtained as final product.

Table 1

Data on U.V. and visible spectra of olefins and carbinols, obtained at room temperature from methylene dichloride solutions.

Compound	λ_{max} (mμ)	ε_{max} (lm^{-1} cm^{-1})	Ref.
Styrene	252	1.73×10^4	30
	(261)	1.16 " "	
	(274)	9.45×10^2	
	282.5	8.59 " "	
	291.5	5.77 " "	
1,1-diphenyl-ethylene	252	1.25×10^4	37
Triphenyl-ethylene	235	~1.8 $\times 10^4$	38
	300	2.15 " "	
	[300]	[2.08 " "]	
Tetraphenyl-ethylene	240	2.70×10^4	38
	291	1.45 " "	
	308	1.50 " "	
Acenaph-thylene	266	2.58×10^3	39
	275	2.40 " "	
	313-315	8.14 " "	
	325	1.02×10^4	
	(332)	~4.1 $\times 10^3$	
	341	4.09 " "	
	389	2.4×10^2	
	410	1.66 " "	
	437	8.67 x 10	
	465	2.51 " "	
Acenaphthyl-ene dimer	256	1.9×10^4	see
	(265)	1.4 " "	
	287	2.9×10^3	
	298	3.3 " "	
	(309)	2.8 " "	
	324	4.9 " "	
	341	9.3 " "	
	360	1.4×10^4	
	378	2.8 " "	
	402	3.3 " "	
N-vinylcarba-zole	245	6.05×10^4	see
	(255-275)	~2.0 " "	
	293	1.88 " "	
	330	4.17×10^3	
	343	4.68 " "	
α-methyl-styrene	244	1.15×10^4	44
	(285)	~2.5 $\times 10^2$	
1,3-diphenyl-butene-1	254-258	1.91×10^4	40
	(265)	1.56 " "	
	284.5	2.05×10^3	
	294	1.17 " "	
1-phenyl-3-methylindane	262	1.0×10^3	41
	267	1.3 " "	
	274	1.0 " "	

Table 1

(Continued)

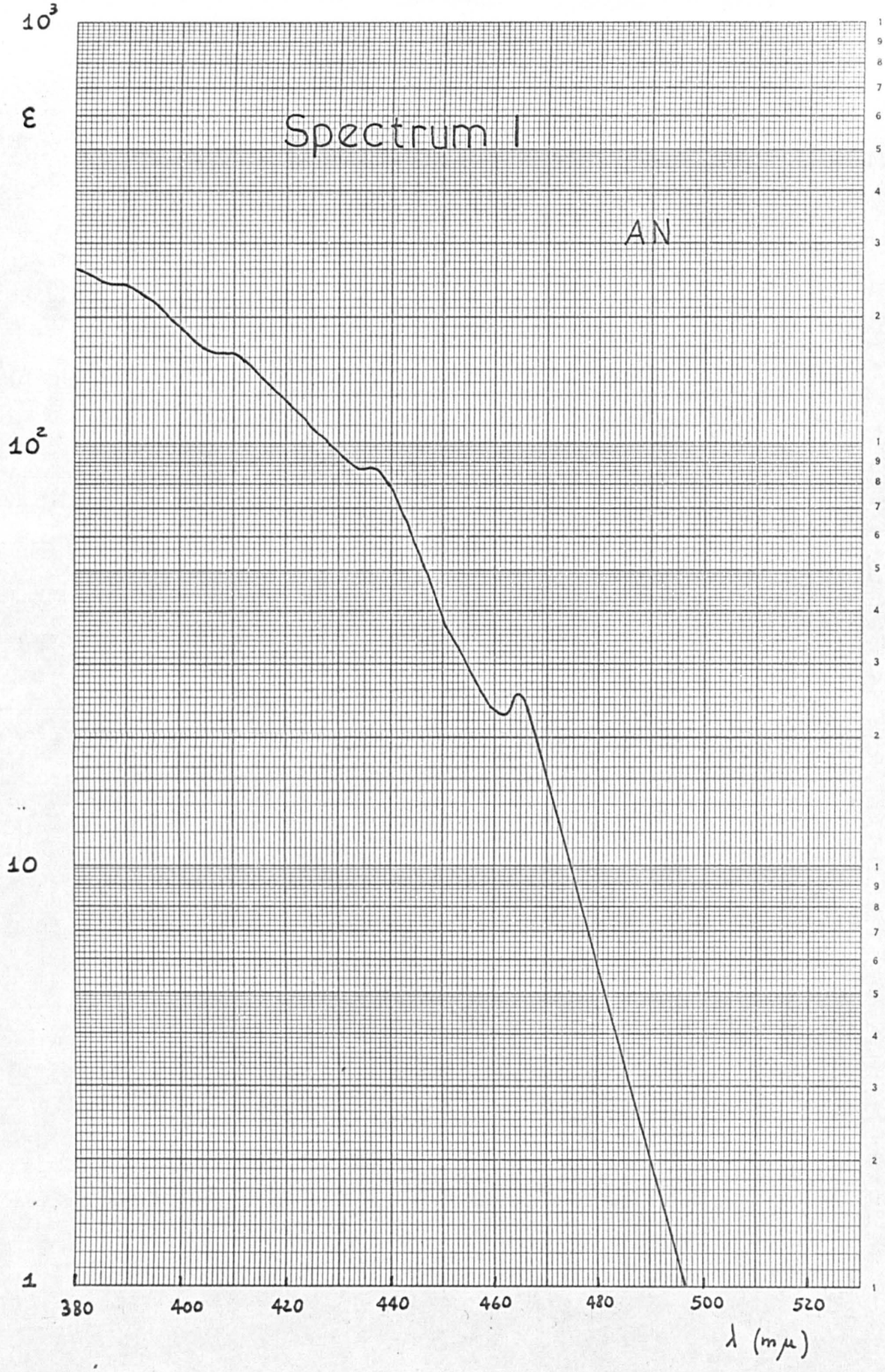
Compound	λ_{max} (mμ)	ε_{max} (lm^{-1} cm^{-1})	Ref.	Compound	λ_{max} (mμ)	ε_{max} (lm^{-1} cm^{-1})	Ref.
1-phenyl-ethanol	253	1.71×10^2	42	1,1,2-triphenylethanol	253	4.30×10^2	※
	258	1.84×10^2	※		258	5.85×10^2	(5)
	265	1.33×10^2	(3)		264	4.70×10^2	
	(267)	$\sim 9 \times 10^1$			(267)	$\sim 3.1 \times 10^2$	
1,1-diphenyl-ethanol	254	4.07×10^2	43	1,1,2,2-tetraphenylethanol	259	1.25×10^3	※
	258	4.85×10^2	※		264	1.25×10^3	(6)
	265	4.00×10^2	(4)		269	8.30×10^2	
	(268)	$\sim 2.9 \times 10^2$					

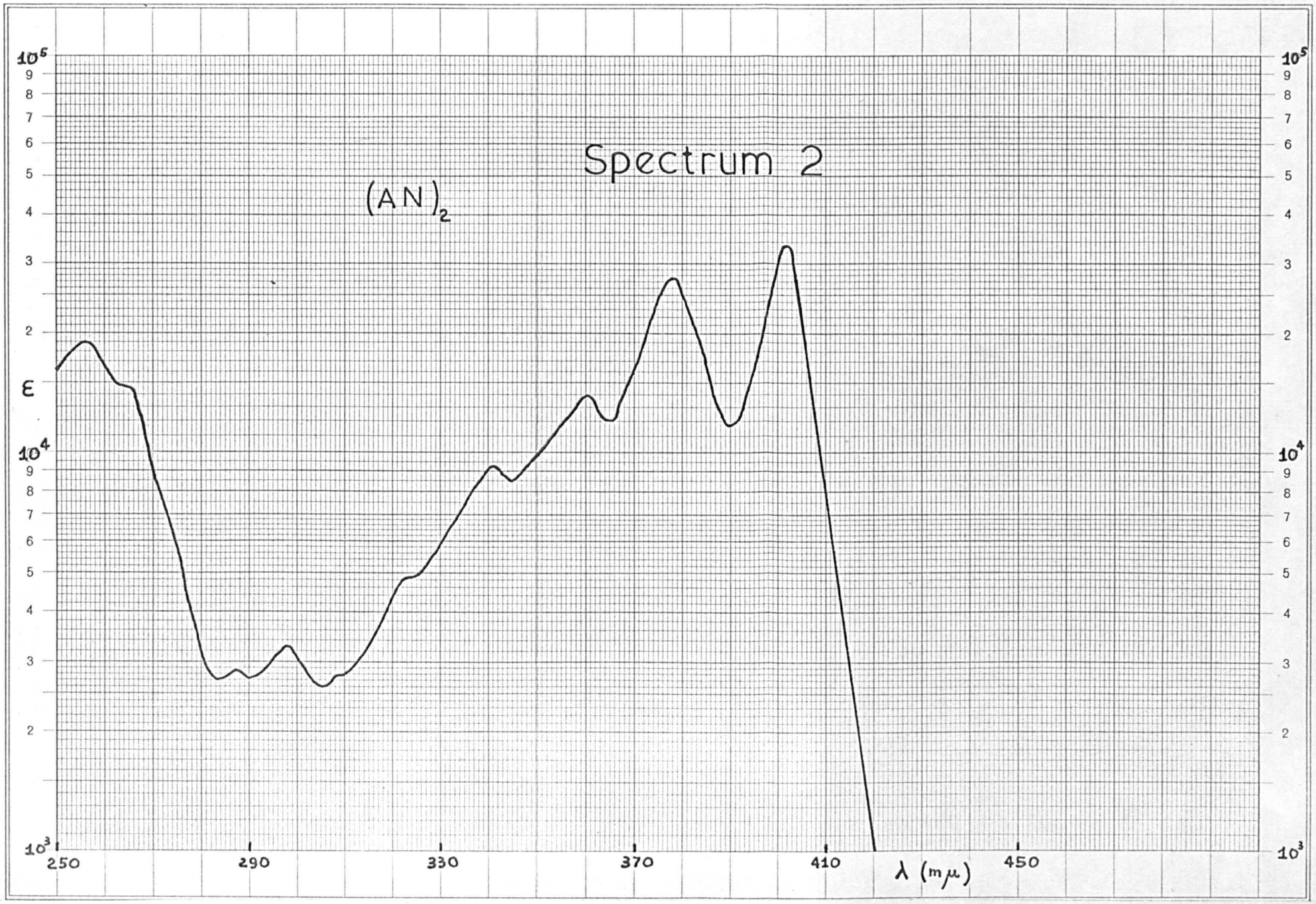
( ) denotes a shoulder;

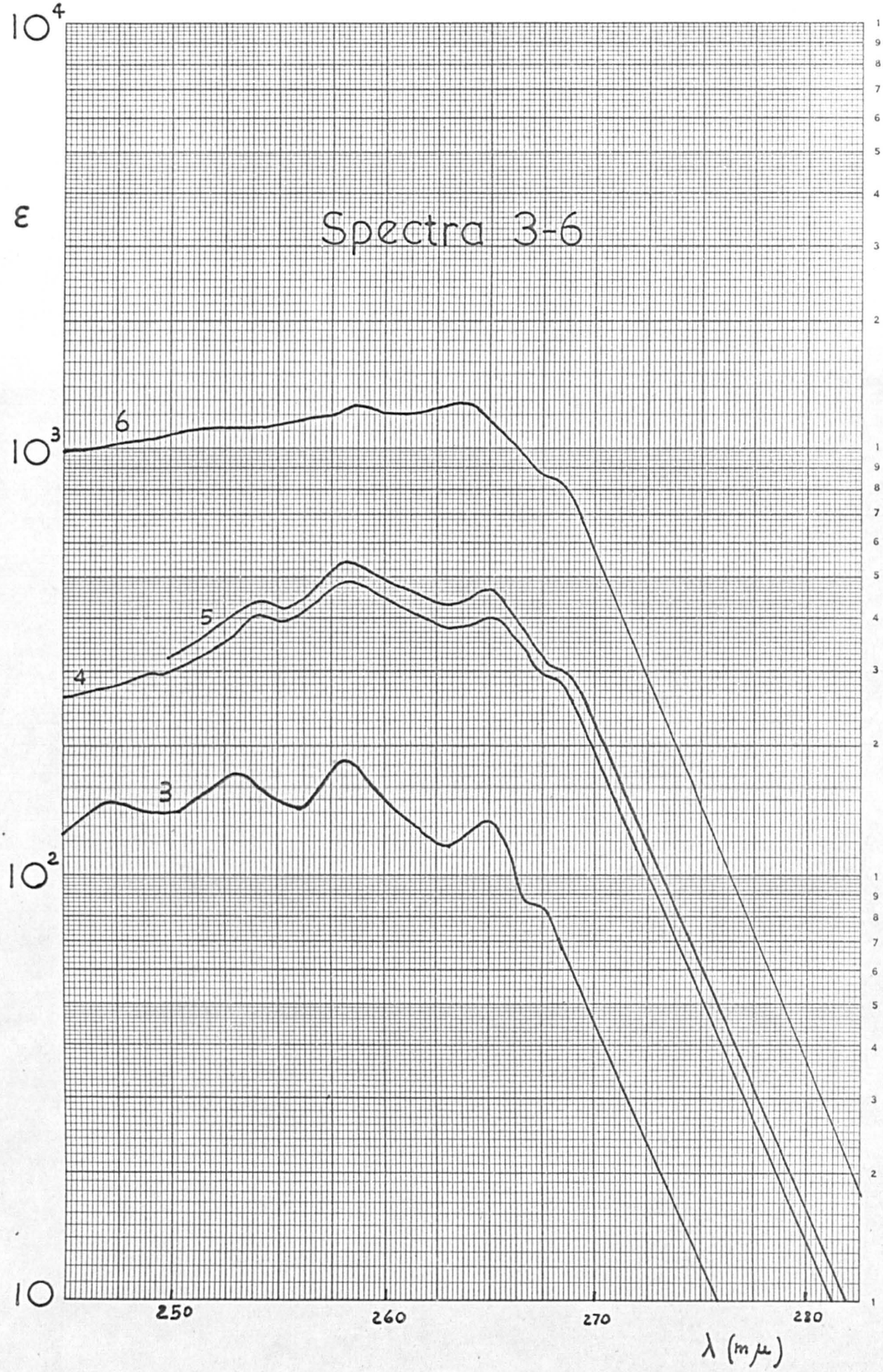
[ ] denotes that the solvent employed was glacial acetic acid;

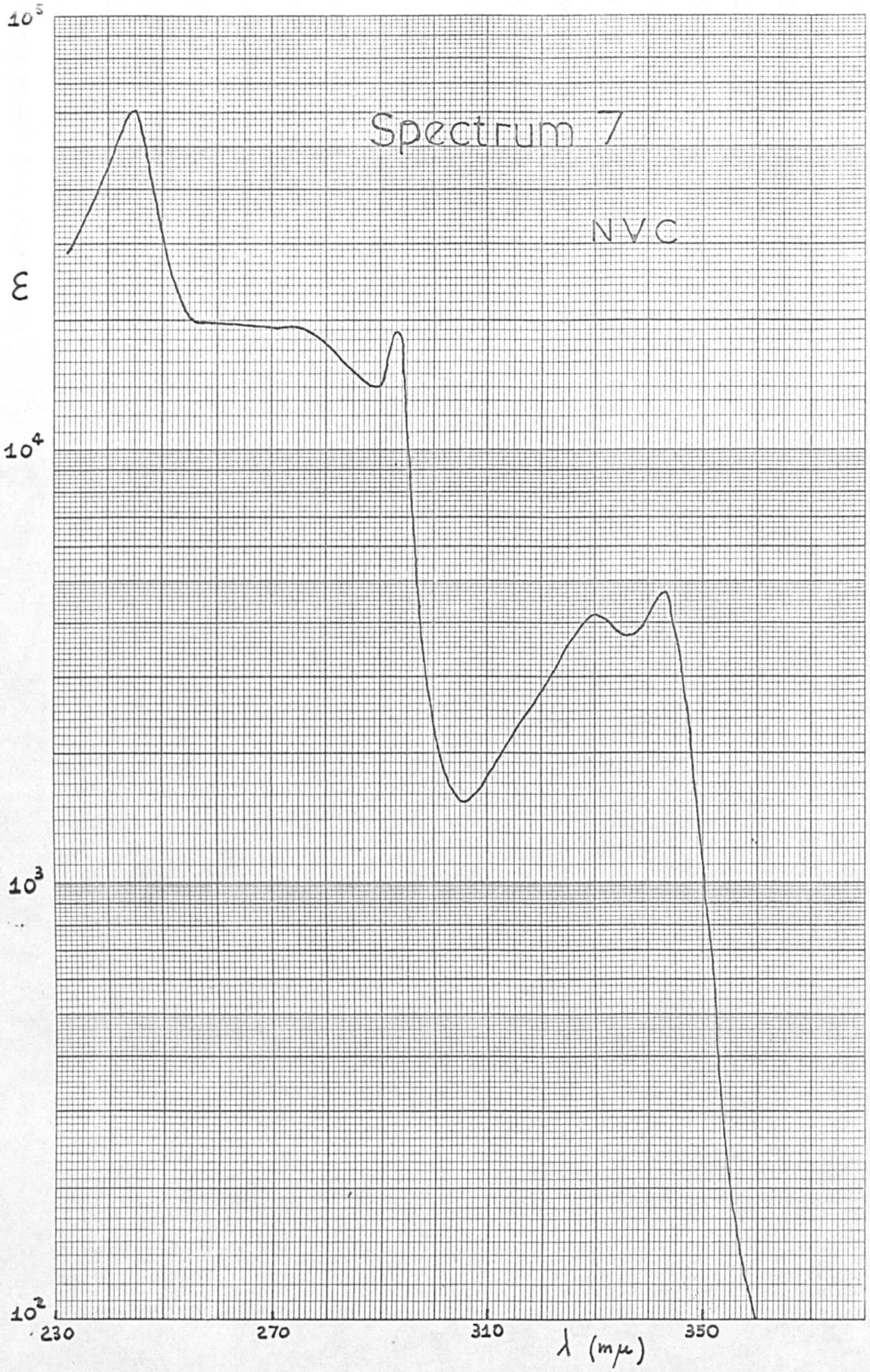
※ the U.V. spectra of the four carbinols are given as Spectra 3 - 6

※※ no reference has been found in the literature for the spectra; of these compounds: they are therefore given in the following pages (Spectra 8 and 7).




Spectrum 2
(AN)2
ε
10^5
10^4
10^3
250
290
330
370
410
450
λ (mμ)





$$CH_2Ph_2 + PhCOPh \xrightarrow{h\nu} CHPh_2.CPh_2OH \qquad III$$

N.B. Table 1 gives data on the U.V. spectra of the four ethanols used.

4. Acids and other catalysts.

4.1 Sulphuric Acid.

AnalaR 98% sulphuric acid, (B.D.H.) was used as supplied for protonation and other open system experiments.

100% B.D.H. sulphuric acid was used for the preparation of phials containing unhydrous solutions in methylene dichloride. The following procedure was adopted (Fig. 4): Approximately 5 ml of 100% sulphuric acid were quickly pipetted into the syphoning flask A through B, B was sealed off and the whole device pumped for a few hours; tap C was then closed and a known amount of solvent ($\simeq$ 15 ml) was run into A. The contents of the flask were frozen and the device sealed off at D. The mixture was allowed to thaw and reach room temperature and good magnetic stirring was then applied for about 15 minutes in order to equilibrate the system. After 3 hours flask A was gently warmed and the upper solvent layer, which was perfectly clear, syphoned into the tipping device (see page 28 , this Thesis). Liquid nitrogen was placed around A and around the tipping flask and the device sealed off at E. The filling of the phials took place after the solution had been allowed to equilibrate anew in the tipping flask at room temperature. The operations

involved in the phial filling will be described in the "perchloric acid" section of this thesis. Of the 12 phials obtained, 2 were crushed under 0.1 N NaOH and the excess of base back titrated with 0.1 N HCl. Consistent results were obtained for the two titrations and the acid concentration thus calculated.

The value for the solubility of sulphuric acid in methylene dichloride at 23° was found to be $1.13 \pm 0.01 \times 10^{-2}$ moles/liter; this is somewhat higher than the solubility in 1,2-dichloroethane (8.95×10^{-3} moles/liter) found by Hayes and Pepper.[11]

4.2 Oleum.

65% B.D.H. oleum was used for the preparation of unhydrous perchloric acid; it was diluted to about 20% SO_3 content with 98% sulphuric acid.

4.3 Trifluoroacetic acid (TFA).

A container of purified acid under its own vapour pressure, provided with a break seal was available in the laboratory from the work of Dr. R. H. Biddulph. This was the starting point for the preparation of phials containing between 0.1 and 20 m moles. The filling of the phials was carried out by high vacuum distillation (Fig. 5); after a thorough pumping out of the device, the system was isolated by sealing off at D. The break-seal B was crushed and some TFA distilled into the first phial of the manifold which was then sealed off at E. The operation was repeated

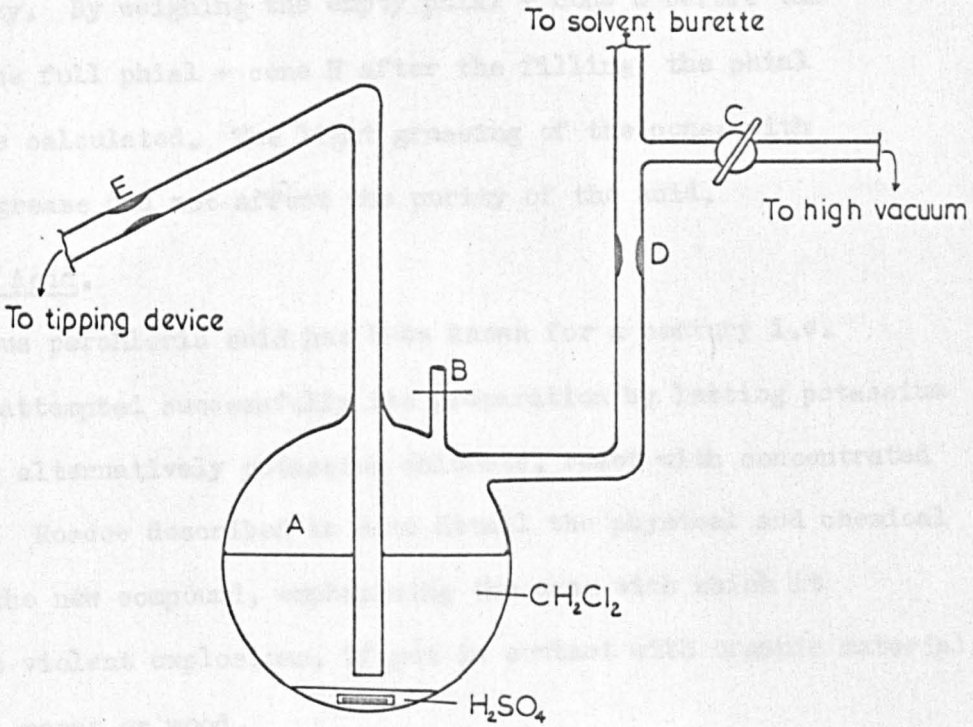


Fig.4 The sulphuric acid phials preparation

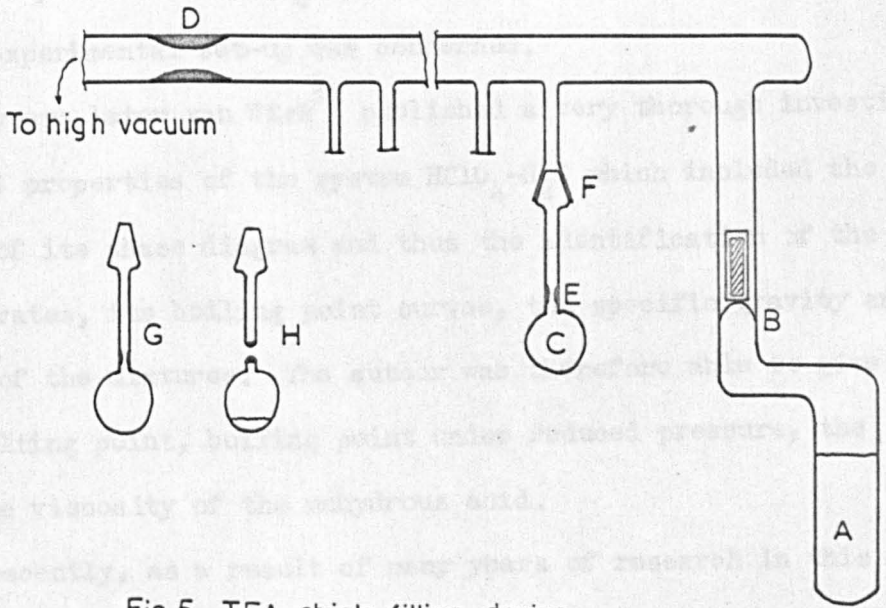


Fig.5 T.F.A. phials filling device

until A was empty. By weighing the empty phial + cone G before the operation and the full phial + cone H after the filling, the phial content could be calculated. The light greasing of the cones with Apiezon vacuum grease did not affect the purity of the acid.

4.4 Perchloric Acid.

Anhydrous perchloric acid has been known for a century i.e. since Roscoe[12] attempted successfully its preparation by letting potassium perchlorate, or alternatively potassium chlorate, react with concentrated sulphuric acid. Roscoe described in some detail the physical and chemical properties of the new compound, emphasising the ease with which it decomposed with violent explosions, if put in contact with organic materials such as cotton, paper or wood.

At the beginning of this century Vorländer and von Schilling[13] described the preparation of $HClO_4$ by a somewhat more sophisticated method, as far as the experimental set-up was concerned.

A few years later van Wick[14] published a very thorough investigation on the physical properties of the system $HClO_4$-H_2O which included the determination of its phase diagram and thus the identification of the different acid hydrates, its boiling point curves, the specific gravity and the viscosity of the mixtures. The author was therefore able to give figures for melting point, boiling point under reduced pressure, the density and the viscosity of the unhydrous acid.

More recently, as a result of many years of research in this field,

Smith[15] published an improved method for the preparation of the unhydrous acid, which consists in mixing commercial 70% $HClO_4$ with 20% oleum in a volume ratio of approximately 1:4. The pure perchloric acid is then distilled off the reaction mixture under reduced pressure and collected in a vessel cooled at dry ice temperature. The acid mixture is warmed slowly up to a final temperature of about 70°. This procedure gives considerably higher yields of $HClO_4$ and does not present any hazard because of the limits within which the temperature is kept.

Tauber and Eastham[16] slightly modified Smith's procedure by preparing $HClO_4$ in a high vacuum, all-glass apparatus; the acid could be dosed into the reaction devices or into breakable phials through a dosing volume.

Table 2 gives an account* of the physical properties of the acid as collected in the literature. $HClO_4$ is a colourless liquid which fumes heavily in air because of the formation of its monohydrate which is solid at room temperature.

Roscoe[12] was the first to observe that the acid, even when kept in the dark, readily undergoes decomposition at room temperature, becoming pale yellow at first, then brown red, and finally almost black. The dark-coloured acid was reported to explode very easily under the effect

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*Zinoviev[16a] has recently published a review on perchloric acid

Table 2

Physical properties of perchloric acid

Melting Point (°C)	Ref.
-112	14
-100	19

Vapour Pressure		Ref.
P(mm)	T(°C)	
18	16	14
2 - 20	-5 - 20	16
39	56	13
$\log P = -\frac{1923}{T} + 7.91$		16a

Density (g/cm^3)	T (°C)	Ref.
1.7676	20	14
1.764	22	13
1.7608	25	36
1.8129	0	26
1.7915	10	"
1.7722	25	"

Viscosity (poise x 10^3)	T (°C)	Ref.
11.89	0	16
9.46	10	"
7.95	25	"

Electrical Conductivity ($mho/_{cm}$ x 10^3)	T (°C)	Ref.
3.619	0	16
3.885	10	"
4.083	25	"

of heating or shaking.

Zinoviev and Tsentsiper[17] have investigated the spontaneous decomposition of $HClO_4$ in the temperature range 40 - 96°; the reaction, which was followed by measuring the rate of oxygen evolution, has an induction period and is initially self accelerating. The temperature dependence of the reaction rate is very strong; thus, for instance, the induction period at 80° is only 5 min. and 1 gr of acid liberates thereafter about 20 cc/min of oxygen; the two figures are reduced at 40° to 480 min. and 0.3 cc/min respectively (volumes at N.T.P.).

I have noticed that even at -3°, the acid slowly decomposes and turns into a yellow-brown liquid within three or four weeks. The pure acid is however completely stable below about -50° and I could not detect any colour in specimens stored at dry ice temperature for several months. The set of reactions given below illustrates how the acid undergoes spontaneous decomposition,[17]

$$3\ HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4.H_2O \qquad \text{IV}$$

$$Cl_2O_7 \rightarrow \tfrac{1}{2}\ O_2 + Cl_2O_6 \quad \text{(red liquid, easily decomposed)} \qquad \text{V}$$

$$Cl_2O_6 \rightarrow O_2 + 2\ ClO_2 \quad \text{(red-brown liquid, explodes readily)} \qquad \text{VI}$$

and in part $\quad 2\ ClO_2 \rightarrow Cl_2 + 2\ O_2 \qquad \text{VII}$

Despite the large amount of work published on the subject, there is still a great deal of disagreement amongst researchers as to

what is the chemical structure of $HClO_4$. Studies of cathodic polarization[18] and phase diagram determinations[19] on the system water-perchloric acid seemed to support the existence and the relative importance of equilibrium IV. More recently however, Dahl and co-workers[20] have shown by Raman spectroscopy that $HClO_4$ in the solid state does not exhibit peaks for Cl_2O_7 and $H_3O^+ClO_4^-$, and thus concluded against the previous interpretation.

It has been found that the acid is not ionized in its pure state, but bears a trigonal symmetry C_{3v} in contrast with ClO_4^- which has tetrahedral symmetry. Additions of small quantities of water to the pure acid produce the transformation of structure. These observations substanciated by many authors[20,21,22] were obtained by comparative measurements of the Raman spectra of $HClO_4$, of aqueous acid solutions and of some perchlorates. They are supported by some data on the electrical conductivity of the $HClO_4 - H_2O$ system,[23] which show that as one approaches the pure acid, the conductivity falls, to reach a minimum, very low value for 100% $HClO_4$.

Perchloric acid forms a great number of addition compounds with water (seven, including the recently discovered $4\ HClO_4.H_2O$[24]), with acetic acid and its halogeno-derivatives,[25] with sulphuric acid,[26] etc. It is soluble in chlorinated hydrocarbons as recently reported by different workers.[16,27,28] Dilute solutions in methylene and ethylene dichloride are perfectly stable at room temperature, in absence of moisture and oxygen

but readily absorb moisture if exposed to the atmosphere and deposit white crystals of monohydrate, which is insoluble in these media. Approximately molar solutions of $HClO_4$ in CH_2Cl_2 were prepared by the technique explained below and were kept for over a year without any sign of deterioration.

The procedure which I adopted for the preparation of the pure acid closely resembled that described by Eastham and Tauber;[16] Fig. 6 illustrates schematically the all-glass apparatus used. After having thoroughly pumped out and flamed the rest of the apparatus, 60 ml of 20% oleum were slowly added to 15 ml of 72% $HClO_4$ (Hopkin and Williams) through the funnel B into the flask A, which was ice cooled. The flask was then sealed off at C, the mixture was frozen and the break-seal E crushed in order to connect the rest of the apparatus and the high vacuum line to the reaction flask. After complete degassing by repeated thawing and freezing of the mixture, the distillation of $HClO_4$ was performed by placing liq. N_2 around F and by warming A progressively from room temperature to 70° in about 5 hours, the dry valves N and P and the metal valve Q being closed. The flask A was sealed off at D at the end of the distillation, the acid was allowed to melt in F and was then fractionally vacuum-distilled. Ganerous head and tail fractions were discarded by sealing them off in their containers H and F, respectively; part of the middle fraction was collected in the microburette M (accuracy $\pm$ 0.003 ml), the rest in the container J, provided with a break-seal L, which was sealed off and stored in liq. N_2 until further use.

The dosing of the acid from M (in which it was stored frozen in the

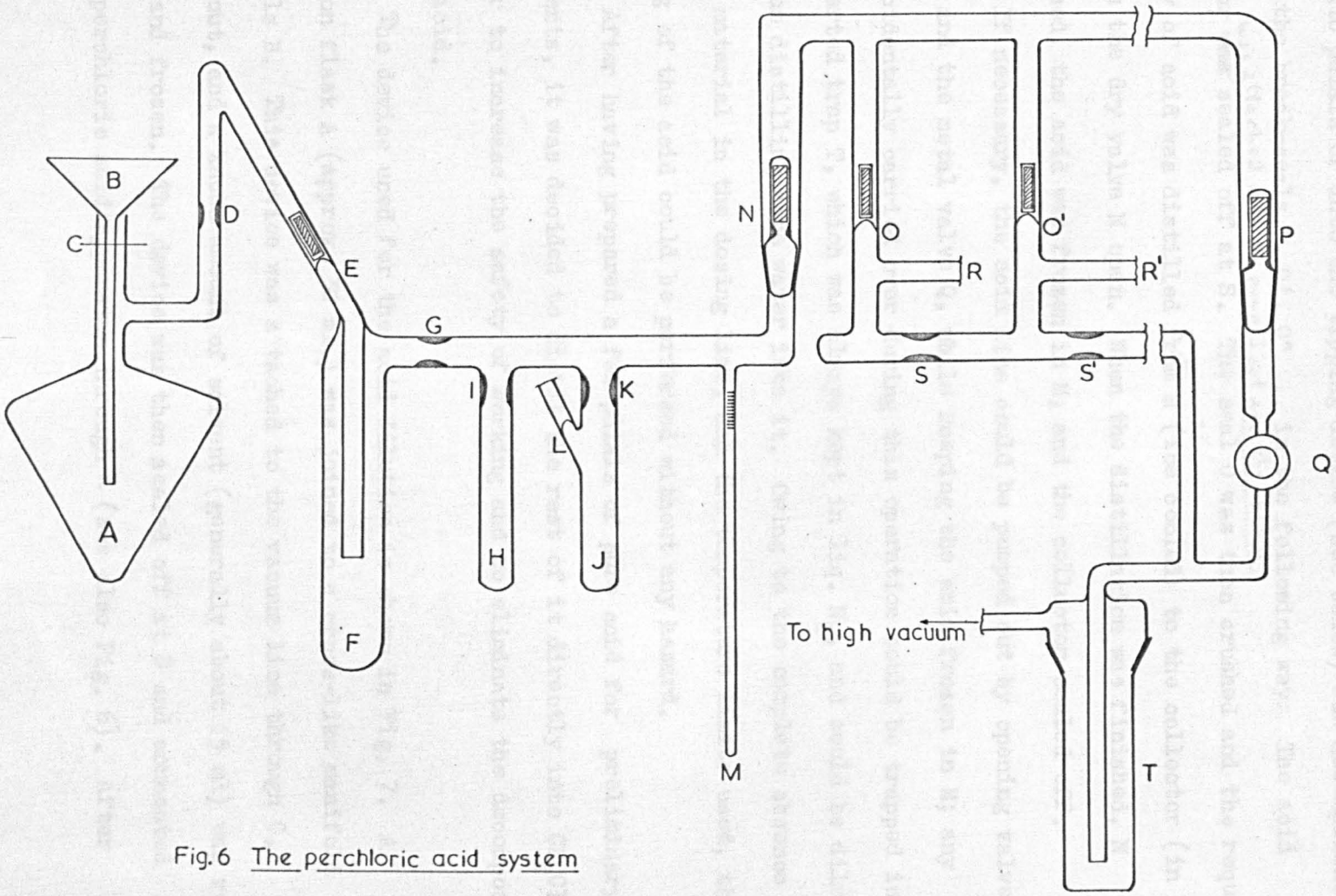

Fig. 6 The perchloric acid system

dark) into phials or into the tipping device (see below) was accomplished through the break-seals 0, 0', 0" ... in the following way: The acid collector ~~was~~ was attached onto R, pumped out and the system sealed off at S. The seal 0 was then crushed and the required quantity of acid was distilled from M (ice cooled) to the collector (in liq. N_2) with the dry valve N open. When the distillation was finished, N was closed, the acid was frozen in M, and the collector sealed off.

If necessary, the acid line could be pumped out by opening valves N and P and the metal valve Q, while keeping the acid frozen in M; any acid accidentally carried over during this operation could be trapped in the inverted trap T, which was always kept in liq. N_2, and could be diluted by vacuum distilling some water into it. Owing to the complete absence of organic material in the dosing line, and the temperature limits used, the handling of the acid could be performed without any hazard.

After having prepared a few phials of pure acid for preliminary experiments, it was decided to distil the rest of it directly into CH_2Cl_2, in order to increase the safety of working and to eliminate the decomposition of the acid.

The device used for the acid dilution is shown in Fig. 7. A small Kon flask A (approx. 30 ml.) was joined to a cross-like manifold of phials B. This device was attached to the vacuum line through C, pumped out, and a known amount of solvent (generally about 15 ml) was run into A and frozen. The device was then sealed off at D and connected to the perchloric acid apparatus through R (see also Fig. 6). After

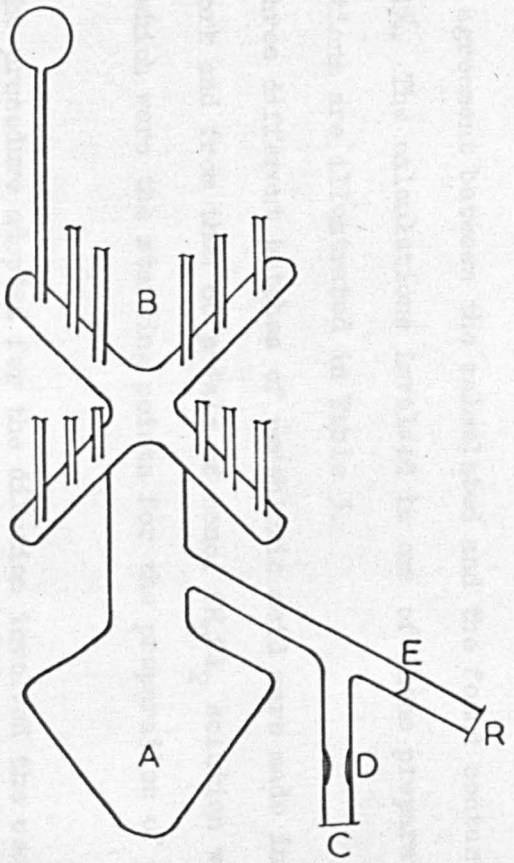

Fig.7 The tipping device

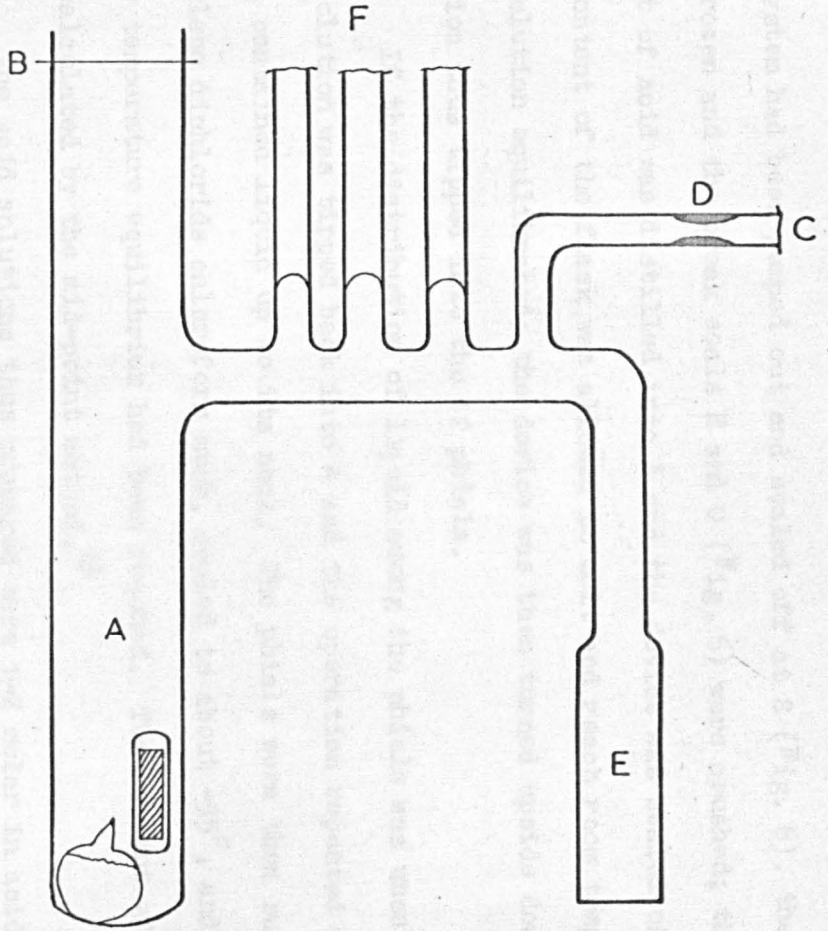

Fig.9 The spectroscopic device

the system had been pumped out and sealed off at S (Fig. 6), the solvent was frozen and the break seals E and O (Fig. 6) were crushed; the desired amount of acid was distilled into A and the device was sealed off at R. The content of the flask was allowed to melt and reach room temperature and the solution equilibrated; the device was then turned upside down and the solution thus tipped into the 12 phials.

If the distribution of liquid among the phials was unsatisfactory, the solution was tipped back into A and the operation repeated until no phial contained liquid up to its neck. The phials were then submerged in a methylene dichloride chloroform mush, cooled to about -95°, and sealed off after temperature equilibrium had been reached. The content of the phials was calculated by the mid-point method.[29]

The acid solutions thus prepared were 1-2 molar in acid; frequent checks on the acid content of the phials were carried out by breaking one of them into an excess of 0.1 N NaOH solution and back titrating with 0.1 N HCl. The agreement between the calculated and the found content was always within $\pm$ 1%. The calculations involved in one of these preparations of acid solutions are illustrated in Table 3.

Three different batches of perchloric acid were made in the course of this work and from them 60 phials of conc. CH_2Cl_2 solution were prepared which were the starting points for the preparation of more dilute ones.

The procedure adopted for the dilution involved the use of the same

Table 3

Calculations and checks on perchloric acid phials.

Phial No.	Wt. Empty Phial (gr)	Wt. Stem (gr)	Wt. ½ Stem + full phial (gr) (vacuum corrected)	Phial Content (gr)	Phial Content (ml at 25°)	Phial Content (mmoles acid)
77	0.5464	2.0508	2.1482	0.5764	0.43	0.286
78	0.4967	1.9502	2.6600	1.1882	0.89	0.590
79	0.5050	1.9264	6.1297	4.6615	3.49	2.315
80	0.5648	1.9798	2.0320	0.4773	0.36	0.237
81	0.5404	2.1454	3.7529	2.1398	1.60	1.063
82	0.4616	2.1338	6.0115	4.4830	3.36	2.226
83	0.5336	2.1937	3.0237	1.3933	1.04	0.692
84	0.5130	2.1065	3.6930	2.1263	1.59	1.056
85	0.4785	2.0089	5.8948	4.4118	3.30	2.187
86	0.4985	2.0080	2.0033	0.5008	0.38	0.249
87	0.4714	1.8668	3.9927	2.5879	1.94	1.286
88	0.4718	1.8797	5.6404	4.2288	3.17	2.100
				tot. = 28.7756		

CH_2Cl_2 run in the device (25°) 20.75 ml ≡ 27.35 gm

$HClO_4$ distilled in the device (0°) 0.800ml ≡ 1.45 gm ≡ 0.0144 moles

28.80 gm

Agreement between values of total weight:

calculated 28.80 gm ; found 28.78 gm

$$\text{Phial content in acid (mmoles)} = \frac{\text{Phial content (gr)}}{28.78} \times 14.4$$

$$\text{Phial content (ml)} = \frac{\text{Phial content (gr)}}{1.335 \text{ (apparent density of solution)}}$$

Titration of phial No. 85: phial crushed in solution containing 3.43 mmoles NaOH; back titration requires 1.23 mmoles HCl.

Found 2.20 mmoles $HClO_4$; calculated 2.19 mmoles

tipping technique; one of the original phials was placed in a large glass tube together with a glass-enclosed magnetic breaker, and then the tube was connected to the tipping device and the solvent vacuum line. After a few hours of pumping, the necessary quantity of CH_2Cl_2 was condensed in the tube, the device sealed off the line, and the phial crushed; the new solution was transferred into the tipping flask, frozen, the tube sealed off, and the solution melted and tipped into the phials.

We prepared thus about 250 phials with an acid content ranging from 5×10^{-4} to 3 mmoles. Checks on phials with very small acid content were performed by spectroscopy as described below.

The phial was placed in a spectroscopic device (see page 34) with a breaker and an excess of triphenylmethyl carbinol, the device was attached to the solvent line, pumped out and filled with a known amount of CH_2Cl_2. After sealing off, the phial was crushed and the visible spectrum of the yellow solution was scanned. It was thus possible to count the number of trityl ion produced and therefore the acid content of the phial.

A typical numerical example of this routine checking is illustrated in Table 4.

The agreement between the expected and the found content was always satisfactory, considering the extremely low acid concentration in the phials.

It is to be noted that these checks provided also a proof that the

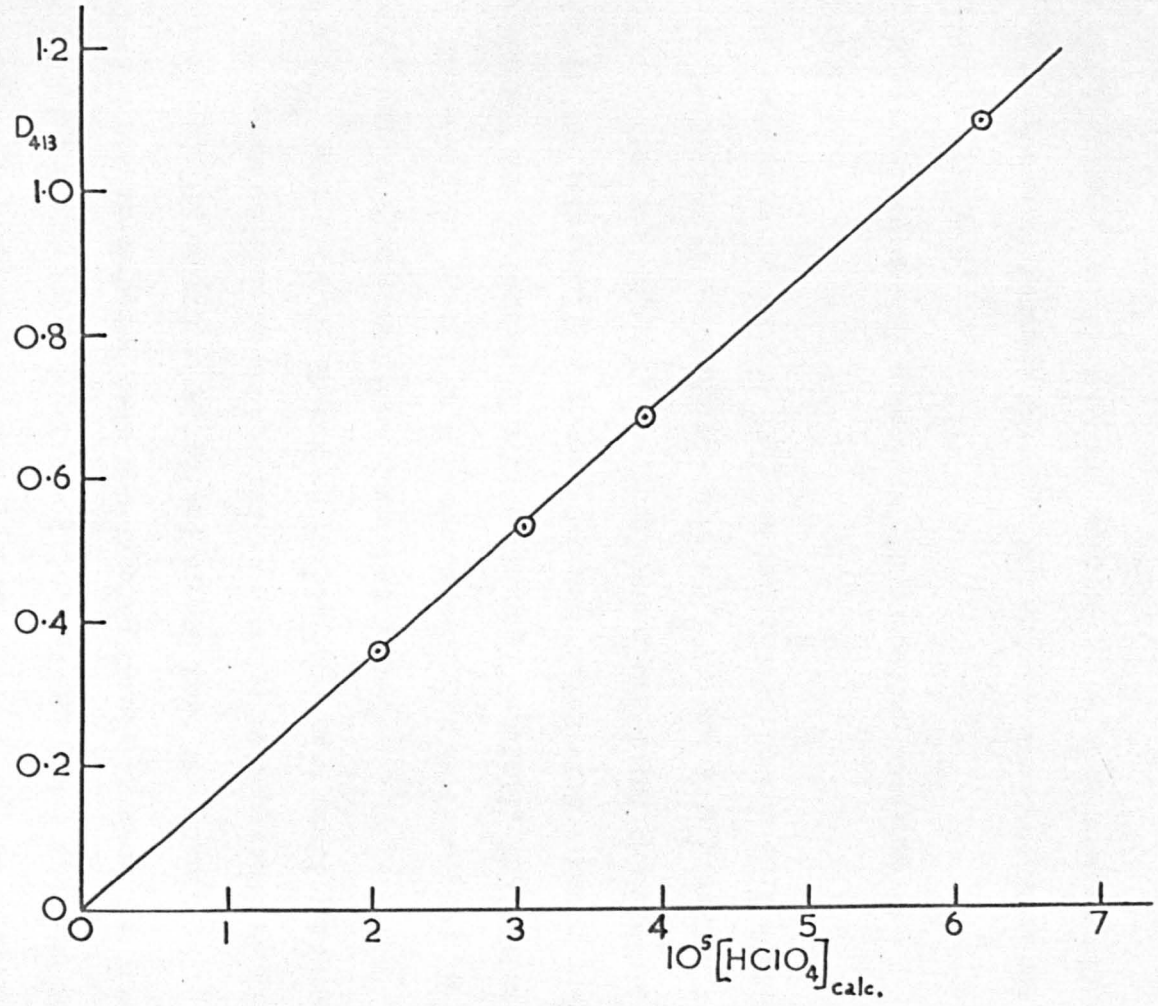

Fig. 8

Table 4

Spectroscopic check on the $HClO_4$ content of a very dilute solution.

Phial used: No. 98, calculated content 0.000661 mmole $HClO_4$ in 0.26 ml CH_2Cl_2

Broken in 10.40 ml of CH_2Cl_2 containing 0.1 mmole of triphenylmethyl carbinol:

$$Ph_3COH + 2\ HClO_4 \rightarrow Ph_3C^+ClO_4^- + H_3OClO_4$$

Then dilutions made according to table below.

Tot. Volume (ml)	Calc. $[HClO_4]$ (10^5M)	D_{413}	Found $[Ph_3C^+] = D_{413}/36{,}400$ (10^5M)	Found $[HClO_4]$* (10^5M)
10.65	6.20	1.097	3.01	6.0 2
17.0	3.89	0.684	1.88	3.76
21.9	3.02	0.530	1.46	2.92
32.1	2.06	0.360	0.989	1.978

* $2[HClO_4] = [Ph_3C^+]$

Error 3%

See also Fig. 8, for the Lambert-Beer plot (opposite).

acid under consideration was still $HClO_4$. Trityl perchlorate is fully ionised in dry CH_2Cl_2,[30] and the spectra of its solutions obey therefore the Lambert-Beer law. By carrying out a few dilutions on the ionic solution under analysis, a good Lambert-Beer plot could be obtained (Fig. 8) (dilutions were performed through break seals attached to the spectroscopic device: see Fig. 9).

It was thus possible to exclude the presence of degradation products such as HCl in the perchloric acid solution, because trityl chloride is only slightly ionised in chlorinated hydrocarbons[31] and would have given a lower ionic absorption, with departure from linear behaviour. Some of these checks were made several months after the preparation of the phials: this proves the complete stability of $HClO_4$ in methylene dichloride.

Other properties of these solutions will be described in the appropriate sections of the thesis.

Solutions of $HClO_4$ in CH_2Cl_2 for use in open system experiments were made up by crushing one of the phials into the required amount of solvent in a conical flask. They were stored as indicated by Reilly,[27] their acidity being frequently checked by titration.

NOTE: It was noticed in some preparations of $HClO_4$ solutions that a violet colour developed on warming the cold solution. This colour turned pale yellow in a few hours and remained such thereafter. Although no appreciable change in the acid content could be detected by analysis, this phenomenon was nevertheless very disturbing considering the effect it would have produced on spectroscopic experiments. After a systematic elimination

of all imaginable causes for this coloration, I found that it was due to some traces of impurities in the distilled water which I used for washing the glassware. This was proved by evaporating to dryness approximately 100 ml of distilled water in a beaker glass, washing it with a few ml of CH_2Cl_2 and crushing a phial of the acid solution: A violet colour developed immediately and then turned yellow.

4.5 Lewis Acids.

Methylene dichloride solutions of $SnCl_4$, BF_3 and $TiCl_4$ contained in anaerobic glass phials were available in the laboratory by the courtesy of Dr. W. Passmann ($SnCl_4$ and BF_3) and Dr. C. J. Panton ($TiCl_4$).

5. Other Reagents

5.1 Silver Perchlorate.

The B.D.H. product was used after thorough drying under high vacuum at about 90°. All reactions involving this compound were carried out in the dark.

5.2 1-Phenylethyl bromide.

This compound, supplied by Estman-Kodak Ltd., was transferred to a flask on the high-vacuum line, degassed and deprived of a first fraction (about 10%) by vacuum distillation at 100°; all the water was thus removed together with all other more volatile impurities. Some of the bromide was then vacuum distilled into breakable phials, the flask and the short distillation path being heated to about 100°.

Before sealing off a phial, the system, now at room temperature,

was pumped out in order to remove small traces of HBr formed by the thermal decomposition of the bromide. No bromide was distilled off during this operation, since its vapour pressure is much less than 1 mm at 20°.

The phials thus obtained contained between 2 and 10 mmoles of the compound (content determined by the mid-point method).[29] Phials with dilute solutions of the bromide in CH_2Cl_2 were prepared by the same diluting-tipping technique described in section 4.4. These contained between 0.02 and 1 mmole of $CH_3.CHPhBr$. Whilst the pure bromide contained in the phials tended to deteriorate turning pale yellow within a few weeks , and was therefore frequently renewed, its CH_2Cl_2 solutions appeared to be quite stable.

PART II: APPARATUS AND PROCEDURES

The most general apsects of the techniques involved in this work are described here; a more detailed account of specific procedures will be given, whenever necessary, in the following chapters in the appropriate context.

1. Spectroscopy.

1.1 Ultraviolet and visible spectroscopy.

The spectra reported in this thesis were taken with a UNICAM SP 700 recording spectrophotometer and occasionally with a UNICAM SP 500 manual instrument. All scanning at fixed wavelengths against time were recorded.

Standard spectra of olefins, carbinols and other stable compounds were taken in 1 cm silica cells fitted with B 7 ground joints. The extinction coefficients were always computed by measuring the slope of a Lambert-Beer plot, drawn through at least three experimental points. For the purposes relevant to this work, it was never necessary to scan at wave-lengths lower than 250 mμ; methylene dichloride, ethylene dichloride, acetic acid and sulphuric acid have transparency limits below this wavelength and could therefore be suitably used; the nitroalkanes were only employed for scanning in the visible region of the spectrum.

All the runs in closed system were carried out with the simple all-glass device illustrated in Fig. 9. The phial to be crushed was

placed in the side tube A together with a glass-enclosed magnetic breaker and, whenever one was used, the desired amount of non volatile reactant. The tube was then sealed off at B and the device was attached to the vacuum line at C.

After the necessary pumping out, the solvent and the other required reactants were distilled into A, cooled to a temperature close to the freezing point of the solvent, and the device sealed off at D. The solution was allowed to reach room temperature and a spectrum of the relevant species taken after some of the liquid had been tipped into the cell E.

The phial was then crushed into the whole of the solution, good mixing being ensured by vigorous shaking. The liquid was quickly transferred into the cell, the device placed into its holder, and the scanning started; a special light-tight lid allowing a large amount of free space above the cell holder, replaced in both spectrophotometers the conventional lid.

Between the moment of mixing of the reactants and the beginning of the scanning 15-20 seconds elapsed.

The minimum volume of liquid required for taking a spectrum with 1 cm cells was about 3 ml; the maximum, compatible with the dimensions of the device and of the cell compartment, was about 30 ml. A tenfold dilution of the reactants could therefore be performed if required.

Dilutions, additions or further quantities of reactants and

introduction of other reactants were easily carried out *in vacuo* through the break seals F.

Pyrex matched cells, 1 cm and 1 mm thick, provided with a sealed-on tube, and 1 cm matched silica cells with silica-to-pyrex graded seals were used as the spectroscopic element of the device just described.

Runs in open system were carried out by mixing the reactants in a small stoppered test tube and quickly transferring some of its content into the cell, which was stoppered and placed in the spectrophotometer. Scanning could be started within about 30 sec. from the mixing.

All spectra, unless otherwise stated, were scanned at room temperature (18-23°).

The minimum and maximum optical densities measureable with a good degree of reliability were 0.008 and 3 respectively, but whenever possible I worked within the limits 0.1 - 1.0 in order to obtain very accurate readings.

The solvents used in the reference cell always came from the same batch as those used for the actual run, and the base lines on the spectrophotometer were adjusted before each run over the whole scanning range with both cells containing pure solvent.

1.2 *Infrared spectroscopy.*

Infrared spectra were recorded with a Perkin Elmer Infracord or with a Perkin Elmer Model 212 depending upon the quality of resolution needed. Conventional techniques were adopted for the preparation of

the compounds to be analysed.

With polymers, transparent films were prepared directly on the rock salt plates by evaporating to dryness a concentrated solution in methylene dichloride.

2. Electrical Conductivity.

The conductivity cell, which was used for experiments in semi-open and closed systems, consisted of an inverted conical Pyrex flask of 500 ml with the electrodes fixed near the bottom (Fig. 10). The two platinum electrodes Pt (1 cm x 1 cm) were placed at about 2 mm distance and held firm by four lead-glass beads Pb (Fig. 10a). The platinum leads attached to the electrodes were spot-welded onto 1 mm thick tungsten rods W which were fused through the walls of the flask and were externally connected to two copper leads Cu. All the external wiring and connections were carefully insulated with a good coating of araldite.

The electrodes were fixed in such a position as to minimise the amount of liquid necessary to cover them (about 15 ml).

A small glass enclosed magnetic stirrer M was placed at the bottom of the flask.

Two ground joints were blown on the upper part of the flask: a B14 cone for attaching the cell to the high vacuum line and dosing system and a B29 socket through which the phial breaking device was introduced. This (Fig. 10b) consisted of a glass rod A, provided with glass enclosed magnetic head B sliding along the vertical axis of the device, which could

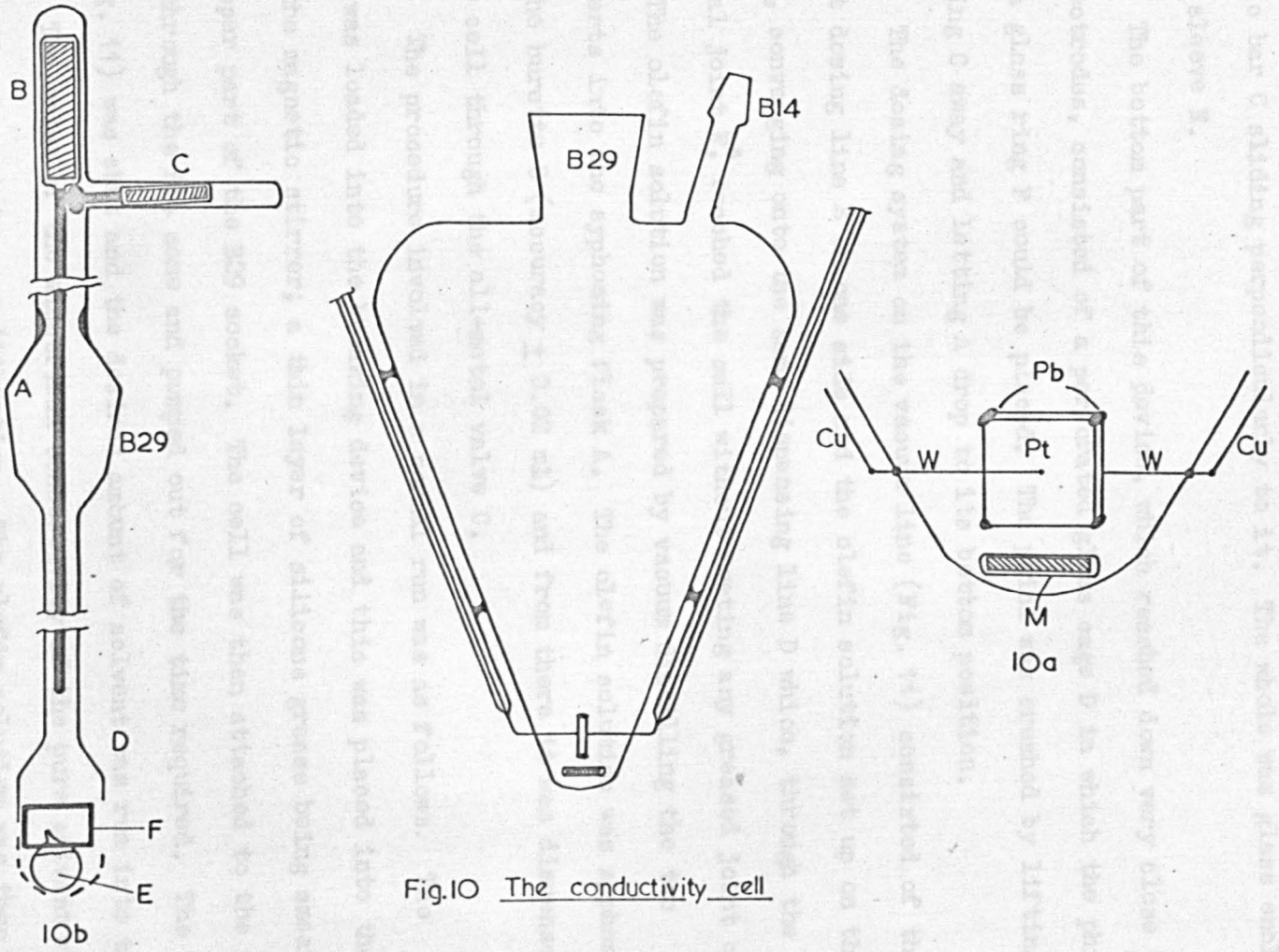

Fig.10 The conductivity cell

be fixed in the top position by making it sit on a small glass enclosed magnetic bar C sliding perpendicularly to it. The whole was glass enclosed in the sleeve E.

The bottom part of this device, which reached down very close to the electrodes, consisted of a perforated glass cage D in which the phial E and a glass ring F could be placed. The phial was crushed by lifting A sliding C away and letting A drop to its bottom position.

The dosing system on the vacuum line (Fig. 11) consisted of the solvent dosing line E on one side and the olefin solution set up on the other, converging onto the same dispensing line D which, through the internal joint F, reached the cell without meeting any greased joint or tap. The olefin solution was prepared by vacuum distilling the two components into the syphoning flask A. The olefin solution was syphoned into the burette B (accuracy $\pm$ 0.02 ml) and from there it was dispensed to the cell through the all-metal valve C.

The procedure involved in a normal run was as follows. The phial was loaded into the breaking device and this was placed into the cell with the magnetic stirrer; a thin layer of silicone grease being smeared on the upper part of the B29 socket. The cell was then attached to the vacuum line through the B14 cone and pumped out for the time required. The tap F'(Fig. 11) was shut and the desired amount of solvent was run into the cell. The value of the electrical conductivity of the pure solvent was taken after temperature equilibration. The olefin solution was then

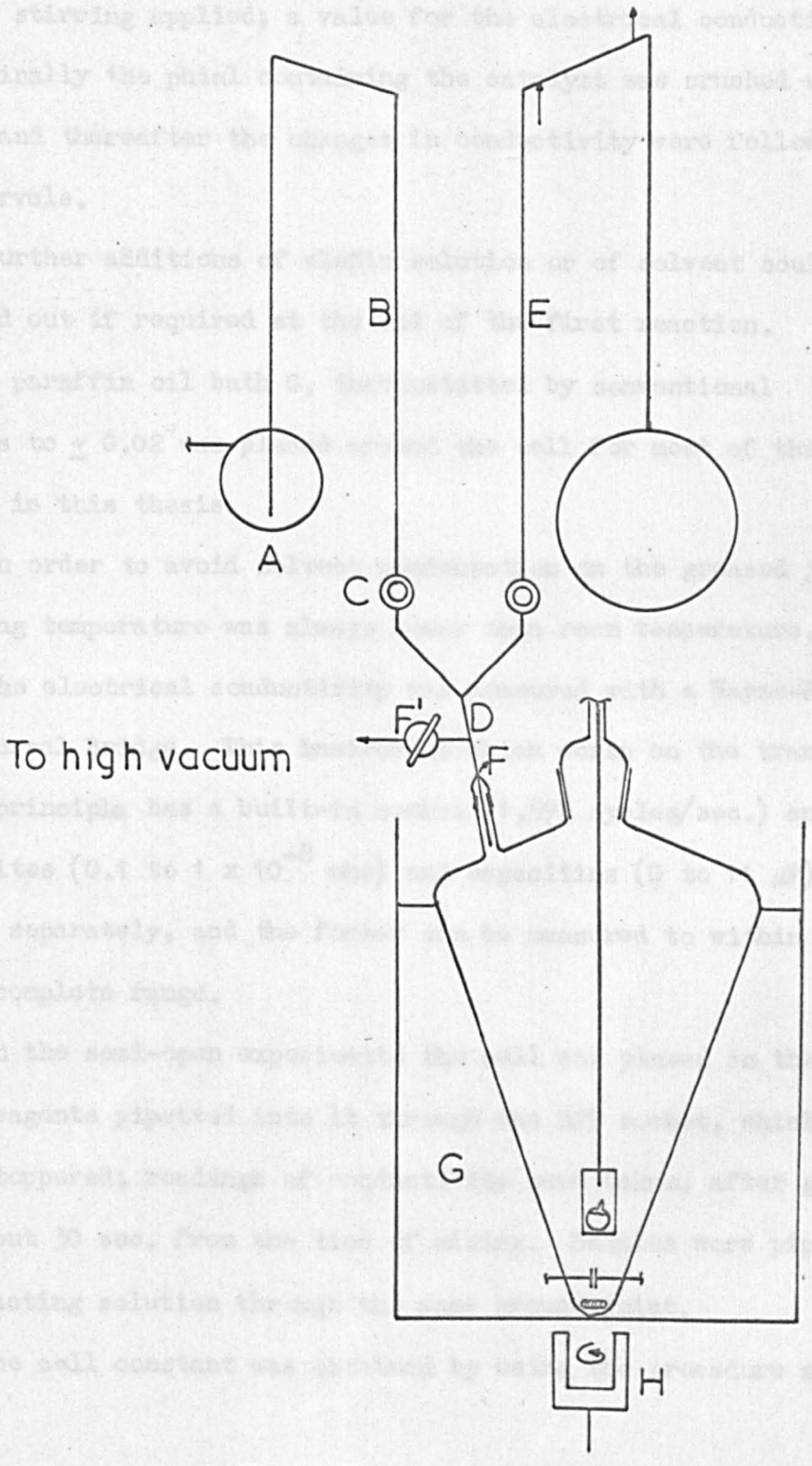

Fig.11 The conductivity assembly

added and stirring applied; a value for the electrical conductivity was taken. Finally the phial containing the catalyst was crushed under good stirring and thereafter the changes in conductivity were followed at close time intervals.

Further additions of olefin solution or of solvent could easily be carried out if required at the end of the first reaction.

A paraffin oil bath G, thermostatted by conventional techniques to $\pm$ 0.02° was placed around the cell for most of the runs described in this thesis.

In order to avoid solvent condensation on the greased joints the working temperature was always lower than room temperature.

The electrical conductivity was measured with a Wayne-Kerr B221 Universal Bridge. This instrument which works on the transformer ratio-arm principle has a built-in source (1,592 cycles/sec.) and detector. Conductivites (0.1 to 1 x 10^{-8} mho) and capacities (0 to 11 μF) are indicated separately, and the former can be measured to within $\pm$ 0.1% over the complete range.

In the semi-open experiments the cell was placed in the oil bath and the reagents pipetted into it through the B29 socket, which was then quickly stoppered; readings of conductivity were taken, after good shaking, within about 30 sec. from the time of mixing. Samples were pipetted out of the reacting solution through the same ground joint.

The cell constant was obtained by using the procedure suggested

by Lind, Zwolenik and Fuoss.[32] Since the conductivity work was confined to a small range of temperatures, it was assumed that the value of the cell constant, determined at 20°, could be applied to all measurements. This was 0.110 $cm.^{-1}$.

We did not correct the conductivities for the resistance of the leads because this contribution was always less than 0.1%.

3. Polymerisation.

The kinetics of polymerisation were obtained by following the reactions calorimetrically. The time-conversion curves were recorded as time-temperature curves, the polymerisations being performed under adiabatic conditions. The apparatus and the procedure used have been described by Biddulph and Plesch[33] and more extensively by Panton.[34]

4. Isolation of polymers.

When the heat production had ceased, the recorder was stopped, air was admitted to the reaction vessel which was then dismantled; its contents were quickly poured into a flask containing a few ml of alcoholic ammonia to neutralise the catalyst.

If the polymer was insoluble in ethanol, the solution from the reaction vessel was poured into an excess of methylated spirit with vigorous stirring; the fine precipitate was filtered off and dried at 50° in a vacuum oven to constant weight. Small glass fragments from the phials were removed with tweezers.

If the polymer was of relatively low molecular weight and therefore partly soluble in ethanol, the neutralised reaction mixture was evaporated under vacuum to constant weight; the amount of impurities derived from the catalyst was generally negligible for yield and viscosity determination.

If a very pure sample of polymer was needed, the polymer was redissolved in a small volume of CH_2Cl_2, the solution filtered (to remove the inorganic residue) and dried anew.

Yields were determined gravimetrically, and whenever the heat of polymerisation was known, they were checked against the values calculated from the temperature rise on the reaction curve, following the standard procedure.[34]

5. Molecular weight determination of polymers.

Molecular weights were determined viscometrically with a pair of Craig-Henderson viscometers by the usual procedure.

For high molecular weight polystyrene, Pepper's[35] relationship:

$$[\eta] = 2.27 \times 10^{-4} \overline{M}_n^{0.72}$$

was adopted.

For low molecular weight polystyrenes ($M_n < 2000$) obtained with perchloric acid as catalyst, we used the more appropriate equation:

$$[\eta] = 2.44 \times 10^{-4} \overline{M}_n^{0.82}$$

obtained by Reilly.[27]

For polyacenaphthylenes and poly-N-vinylcarbazoles, for which the relation between molecular weight and intrinsic viscosity is not known, an internal comparison of $[\eta]$ values replaced molecular weight comparisons.

All viscosities were measured in benzene at 25°. *

6. Vapour phase chromatography.

Two different instruments were used to analyse the purity of materials. Volatile compounds (solvents and some of the olefins) were passed through a Perkin Elmer Model 451, standard columns and procedure being adopted.

For substances of high boiling point, an instrument working at high temperatures, provided with an ionizing detector, was used. The compound to be analysed was dissolved in a volatile solvent (diethylether or benzene) to form an approximately 1% solution which was injected into the instrument.

I am grateful to Dr. J. Jones of Keele University for giving me the opportunity of using the latter chromatograph.

7. Other techniques.

Melting points, refractive indices, and other routine determinations were performed by standard techniques.

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*At a later stage, however, values of $\bar{M}_n$ for low molecular weight polystyrenes were redetermined using the MECROLAB Vapour Pressure Osmometer Model 301A. The calibration curve was constructed with tetraphenylethylene as standard compound and benzene as solvent. The vapour pressure technique gives more reliable and more accurate results than viscometry for low values of $\bar{M}_n$ (200 - 2000).

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CHAPTER TWO

THE INTERACTION OF AROMATIC CARBINOLS WITH ACIDS

1. Introduction.

As mentioned previously in this thesis (p. 2), one of the conventional ways of obtaining stable carbonium ions consists in dissolving a carbinol in a strong acid:

$$R'R''R''' COH + 2\ HA \rightarrow R'R''R''' C^{+} + H_3O^{+} + 2\ A^{-}$$

Sulphuric acid is the most commonly used ionising agent, but other acids have also been employed. A thorough study of the basic properties of several triarylmethyl carbinols and of the spectral characteristics of the corresponding carbonium ions has been published by Evans and co-workers,[1] who used 100% formic acid as reaction medium. The carbinols were found to ionise in this acid to an extent which was proportional to their relative basicity. The visible spectra of solutions of these carbinols in 98% sulphuric acid were taken as reference standards.

In studies concerned with olefinic carbonium ions it has been common practice to conduct parallel spectroscopic investigations of the species obtained by dissolving a given olefin and its corresponding carbinol in concentrated sulphuric acid. The identity of the two spectra was taken as proof of the presence of carbonium ions in the olefin solution, and it was concluded that other species (such as π-complexes) were not formed.

Jordan and Treloar[2] recurred to this arguement in order to show that 1-phenylethyl carbonium ions were formed when styrene was dissolved in 98% sulphuric acid; the spectrum of this solution was in fact almost identical with that of a solution of 1-phenylethanol in the same medium.

An analogous mechanistic interpretation was proposed by Grace and Symons[3] in a study of the spectra of aromatic carbonium ions obtained under similar conditions.

The scope of our investigation was essentially to obtain some information on the u.v. and visible spectra of the carbonium ions derived from the following carbinols:

$CH_3.CHPhOH$, $CH_3.CPh_2OH$, $CH_2Ph.CPh_2OH$, $CHPh_2CPh_2OH$

using perchloric and sulphuric acid as ionising agents.

For the reasons discussed above, I thought it would be useful to study the spectroscopic behaviour of these systems before starting an investigation on the interaction of the corresponding olefins with acids.

2. Perchloric acid and carbinols.

All the work involving $HClO_4$ was carried out in the high vacuum spectroscopic devices described in the experimental section of this thesis (p. 34); 1 cm silica cells were used. Reactions were performed at room temperature (18-23°), and the solvent used was methylene dichloride.

Solutions of the carbinol were made up under vacuum in the device; concentrations were computed from the u.v. spectra recorded before the reactions. The reactions were then started by breaking a phial containing the perchloric acid solution. Scanning could be started, as already mentioned, 15 - 20 sec. after the mixing of the reactants.

2.1 1-phenylethanol.

When solutions of this carbinol ($3 - 5 \times 10^{-4}$ M) were treated with a large excess of $HClO_4$ ($3 - 6 \times 10^{-2}$ M), a yellow colour was produced, which deepened in the first minute or two after the mixing. A single peak was found in the visible region at 428 - 429 mμ; the rate of increase in optical density at this wavelength was recorded in two experiments and was found to be of first order overall, in good agreement with the corresponding rate of protonation found for the reaction between styrene and perchloric acid. (See Chapter 4). Owing to the large excess of perchloric acid, secondary reactions played an important part in this system; after having reached a maximum value, D_{428} remained constant for a few minutes, then started to decrease slowly, whilst a strong absorption band developed at ca. 250 mμ. It was however possible to compute a figure for the molar extinction coefficient of the absorption maximum, viz. $\varepsilon_{428} = 4.0 \pm 0.2 \times 10^3$, on the assumption that all the carbinol had been ionised to the 1-phenylethyl carbonium ion.

Full details on the rate of formation and on the u.v. and visible spectra of the 1-phenylethyl carbonium ion will be given later below. Three runs were carried out with this system.

When the carbinol ($5 \times 10^{-4} - 2 \times 10^{-3}$ M) was made to react with a slight excess of $HClO_4$, by the time the first spectrum was taken, an equivalent amount of styrene had been formed; the solution then turned faint yellow and its visible spectrum showed the presence of a broad

peak centred at about 425 mμ. The styrene formed polymerised to a mixture of oligomers, as shown by the u.v. spectra frequently scanned, and by a spectrum of the material recovered after the end of the reaction. Two runs were performed under these conditions.

Finally, when the carbinol ($\simeq 10^{-3}$ M) was treated with small quantities of $HClO_4$ ($\simeq 10^{-4}$ M), dehydration to styrene occured rapidly enough to be complete by the time the first spectrum was recorded. Polymerisation of the olefin followed the dehyration, but no absorption in the visible region of the spectrum could be detected under these conditions. Two runs were carried out on this system.

2.2 1,1-diphenylethanol.

Small quantities of perchloric acid (to give solutions approximately 10^{-4} M) were found to dehydrate rapidly, i.e. within 20 - 30 sec., 5 or 10 times their amount of 1,1-diphenylethanol to 1,1-diphenylethylene. Two runs were carried out on this system.

2.3 1,1,2-triphenylethanol.

Two reactions were carried out between this carbinol and $HClO_4$ under the conditions reported for 1,1-diphenylethanol. Again, by the time the scanning was started, all the carbinol had been dehydrated to triphenylethylene.

2.4 1,1,2,2-tetraphenylethanol.

Four runs were carried out to investigate the reaction between this carbinol and perchloric acid. The acid concentration was

$1 - 3 \times 10^{-4}$ M and the ratios [carbinol]/[acid] were 0.7, 2.0, 3.5 and 7. In the first run, after the fast dehydration of the alcohol to tetraphenylethylene, a small peak slowly developed in the visible region at 491 mμ; its origin will be discussed in Chapter 3. The other three runs produced a rapid dehydration to the olefin, the reaction being complete before the scanning of the first spectrum. No colour developed in the solutions, which were left for about 24 hours before being disposed of.

Note: As can be seen from the data in table 1, Chapter One, the olefins under consideration always have absorption bands at wavelengths where the corresponding carbinols do not absorb at all. Owing to these remarkable spectral differences, the computation of the olefin concentration from the first spectrum scanned after the mixing of the reactants was easy and unambiguous. Good agreement was always found between the initial quantity of carbinol and the corresponding quantity of olefin produced from it by the dehydration reaction.

3. Sulphuric acid and 1,1,2-triphenylethanol.

Several reactions were carried out between these two compounds in glacial acetic acid. Dilute solutions of the carbinol in AcOH were added to the required amount of a mixture of H_2SO_4 and AcOH and the resulting solutions were quickly transferred to 1 cm silica cells; these were stoppered and the spectra taken.

Addition of sulphuric acid to 10^{-5} - 10^{-4} M solutions of the carbinol, to form solutions 1 - 6 M in sulphuric acid, resulted in a rapid and complete dehydration of the carbinol to triphenylethylene; no carbonium ions were subsequently formed, and these solutions remained colourless for about 24 hours, after which they still exhibited the same u.v. spectrum of the olefin.

At sulphuric acid concentrations between 6 and 9 M, the carbinol was again dehydrated in less than 30 sec, but the triphenylethylene formed was then slowly ionised, and the solutions turned yellow-green. When the concentration of sulphuric acid exceeded 9 M, it was virtually impossible to record a spectrum of the olefin, for its protonation was then very rapid.

Since the colour formation in these reactions always followed the dehydration, and was therefore due to some reaction between the olefin and the acid, the description of these experiments and the discussion of the results will be given together with those relating to the interaction of triphenylethylene with acids. (Chapter Three).

4. Acetic acid and 1,1,2-triphenylethanol.

Solutions of 1,1,2-triphenylethanol in glacial acetic acid (5×10^{-4} - 5×10^{-2} M), although apparently stable for a few days, were checked after several months' storage. Their spectra showed the presence of triphenylethylene. A solution 5.1×10^{-4} M was tested 10 months after its preparation and showed that 50% of the carbinol had been converted into the corresponding olefin. (The solutions were kept in stoppered bottles

in the dark).

5. Discussion.

The above results concerning the dehydrating action of $HClO_4$, H_2SO_4 and AcOH upon the carbinols, is of considerable importance for the problems of carbonium ion preparation. The arguments based upon the similarity of spectra obtained from acidic media containing an olefin and the corresponding carbinol, seem now untenable. In both cases one is in fact dealing ultimately with the same system (olefin + acid), and it is therefore obvious that similar results would be obtained. These findings made it useless for this work to be continued, since they disproved the very principle on which it had been started.

It is interesting to notice that when the quantities of water liberated by the dehydration reaction are higher than the acid concentration, i.e. when the ratio [carbinol]/[acid] is higher than 1, no carbonium ions are produced; this shows the high sensitivity of these species even to small quantities of water. Therefore, in view of the fact that the dehydration reaction promoted by perchloric acid is truly catalytic, and proceeds to completion even with a molar ratio carbinol to acid of ten, it is very difficult to accept the carbonium ion mechanism proposed by La Vonne[4] for the systems 1,1,2-triphenyl- and 1,1,2,2-tetraphenylethanol - acetic acid - perchloric acid.

This author followed spectroscopically the dehydration of these carbinols to olefins, using an excess of perchloric acid (2 - 50 times).

The reactions were fairly slow (half life 30 - 60 min. at 30°) and of pseudo-first order throughout. The reaction mechanism proposed is illustrated below for a "dry" and a "wet" system.

$$ROH + H^+ \underset{}{\overset{K}{\rightleftharpoons}} ROH_2^+ \quad \text{(fast)}$$

$$ROH_2^+ \xrightarrow{k} R^+ + H_2O \quad \text{(slow)}$$

$$R^+ \rightarrow \text{olefin} + H^+ \quad \text{(fast)}$$

(for "wet" system substitute H_3O^+ for H^+)

$$\text{Rate} = k[ROH_2^+] = kK\,[ROH][H^+]$$

The author found the reaction to be of 1st order both with respect to carbinol and to acid. No mention of any colour of the reacting solutions can be found in this work.

In the light of the results presented in this chapter, such an interpretation seems rather unlikely. The low rates of dehydration found by La Vonne, compared with mine, might be due to:

a) The relative basicity of acetic acid, which is known to form addition compounds with perchloric acid;[5] these would obviously be much less effective dehydrating agents.

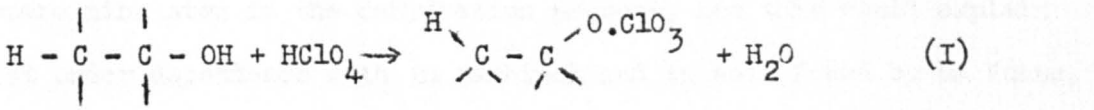
b) The presence of considerable quantities of water in the reaction media (water was in fact found to have a strong retarding effect on the reaction.)

It is likely that both factors played a role in retarding the reactions, but the first seems to have been the determining one.

Both La Vonne's and my results can be interpreted on the basis of a series of reactions involving ester molecules rather than carbonium ions, as shown below.

The reactions will be written for the perchloric acid case, on the understanding that they apply equally well to systems involving sulphuric and acetic acid.

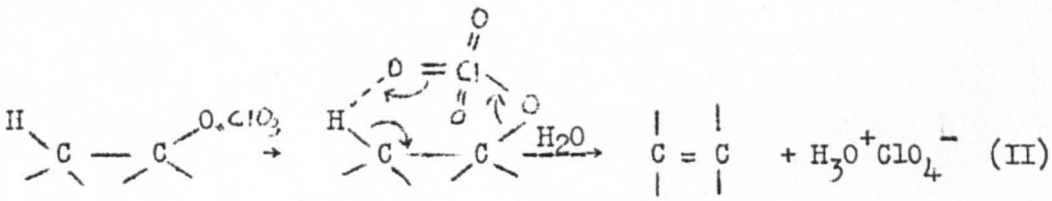
The carbinol reacts with $HClO_4$ to give the corresponding ester:



(I)

N.B. When the reaction is carried out in acetic acid, as in La Vonne's case, the perchloric acid is present in the form 2 $CH_3COOH.HClO_4$.[5]

The ester then undergoes a cyclic <u>cis</u>-elimination with formation of the olefin and the acid hydrate:



(II)

The acid hydrate can interact with more carbinol and thus catalyse further its dehydration to olefin, through the same set of reactions.

There is a close similarity of mechanism between these reactions and those involved in the preparation of olefins by the Chugaev

cis-elimination method.[6] In both cases an ester molecule, prepared from the corresponding alcohol, eliminates acid by passing through a six-membered cyclic transition state, and thus yields the olefin.

In view of the fact that the carbonium ion mechanism is not tenable in this case, as discussed above, the ester interpretation proposed seems to be the most plausible. Moreover, this is supported by all the evidence we have obtained of the existence of perchlorate esters, which will be presented in the following chapters.

In the presence of acetic acid, reaction I is most probably the rate determining step in the dehydration process, and this would explain the first order dependence both in carbinol and in acid found by La Vcnne, and the retarding effect of added water.

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CHAPTER THREE

THE INTERACTION OF UNPOLYMERISABLE OLEFINS WITH ACIDS

1. Introduction.

The reasons which induced me to conduct some experiments on the interaction of unpolymerisable olefins with acids have already been given.

The choice of the two particular olefins was dictated by the following considerations:

Triphenylethylene (3PE) has received some attention in the past. Gold and Tye[1] have reported the u.v. and visible spectrum of its proton adduct in concentrated sulphuric acid. More recently Kohn[2] has found that 3PE turns green-brown when put in contact with acid clays. It has generally been assumed, since Gold and Tye's publication, that 3PE should behave towards protonating agents in the same way as 1,1-diphenylethylene (2PE); the long wavelength peak (around 600 mμ) which is exhibited by spectra of weakly acidic solutions containing 2PE has however, never been reported for 3PE. Since the nature of the species responsible for this peak has raised a considerable amount of discussion,[3] an investigation of the behaviour of 3PE in acidic media of variable strength promised to be of interest. Moreover, the use of 3PE eliminated one complication typical of systems involving 2PE and acids, viz., the formation of dimer.

Tetraphenylethylene (4PE) is insoluble in sulphuric acid and the only evidence of its interaction with acids was provided by Evans and co-workers[3a]

who simply gave the absorption maxima of spectra obtained from solutions of this olefin in benzene and nitrobenzene in the presence of trichloroacetic acid. The study of the interaction of 4PE with perchloric acid was therefore expected to yield some valuable information.

The techniques employed for the spectroscopic and the conductimetric experiments to be described have been discussed in Chapter 1.

2. 3PE and acids.

2.1. 3PE and sulphuric acid.

The interaction of 3PE with excess sulphuric acid was studied by spectroscopy, using acetic acid as third component. A series of mixtures of the two acids was prepared and these were stored in stoppered flasks. An aliquot of a stock solution of the olefin in acetic acid was then added to each mixture, the resulting solutions were shaken, and spectra were taken at appropriate time intervals during several hours; the volume of olefin solution was always a very small fraction of the total resulting volume. This procedure minimised the heat evolution due to the mixing of the acids, and side reactions, such as sulphonation of the benzene rings, were thus reduced.

Three complete series of runs were carried out at room temperature with olefin concentrations (constant for a given series) ranging between 3×10^{-5} and 5×10^{-5} M. Each series consisted of seven runs with increasing sulphuric acid concentration.

A fourth series of runs was performed with 1,1,2-triphenylethanol

instead of 3PE; the results obtained from this were identical to those obtained with 3PE, for the reasons already given (see Chapter Two).

Since the variation in 3PE concentration within the limits studied did not bring any appreciable change in the behaviour of the system, the findings reported below refer to the whole work carried out; I have grouped them according to the determining variable, viz., the molar ratio [sulphuric acid]/[acetic acid], (R).

a) $20 > R \geqslant 5$ ($[H_2SO_4]$ = 18-15 M). The protonation of the olefin was virtually instantaneous. The initial spectrum of the solutions, obtained by the extrapolation technique used by Gold and Tye,[1] was that of the carbonium ion (I). The table below gives the data relating to this spectrum compared with those found by Gold and Tye.[1]

	λ_{max} (mμ)	ε_{max} (calculated on the assumption that all the olefin is protonated)
Present work	316	$9.0 \pm 0.5 \times 10^3$
	430	$2.0 \pm 0.1 \times 10^4$
Reference 1	316	9.5×10^3
	430	2.5×10^4

$CH_2Ph.\overset{+}{C}Ph_2$

I

No other peaks were detected. The changes of the spectrum with time followed the same pattern as those

reported by Gold and Tye, but occurred more rapidly (D_{430} was reduced to half its initial value within about 30 minutes).

b) $5 > R \geqslant 2$ ($[H_2SO_4]$ = 15-12 M). The reaction mixtures behaved in the same way as in a), but a small peak at 660 ± 2 mμ appeared in the spectrum from the beginning; its optical density did not change with time, contrary to the rest of the spectrum. D_{660} was smaller than 1/10 of the initial D_{430} for R = 5, and smaller than 1/3 of it for R = 2. Only a fraction of the olefin was protonated (60-80%).

c) $2 > R \geqslant 1$ ($[H_2SO_4]$ = 12-9 M). The initial spectrum of these solutions remained unchanged for over two hours. In the u.v. the olefin peak was still present, but slightly displaced (310 mμ instead of 300 mμ); its optical density was about 2/3 of what it would have been if there had been no ionisation. In the visible region, the carbonium peak at 430 mμ was reduced to a very small peak (D_{430} = 0.04 - 0.08), whilst the long wavelength peak had become fairly important ($D_{660} \simeq 0.2$).

d) $1 < R \leqslant 0.5$ ($[H_2SO_4]$ = 9-6 M). The olefin was protonated slowly as shown by the changes in D_λ with time referred

to the olefin peak in the u.v. and to the carbonium ion peak in the visible. These are illustrated in Fig. 12 together with the changes in D_{660} which follow a similar pattern.

e) $0.5 < R < 0$ ($[H_2SO_4] = 6\text{-}0$ M). No detectable reaction took place during the first 24 hours following the mixing. The u.v. spectrum of these solutions remained that of 3PE throughout, with D_{300} at its original value. No peaks were detected in the visible region of the spectrum.

The reproducibility was rather satisfactory for these experiments; the scatter was always contained within $\pm$ 5% , both in optical density and in rate measurements.

An approximate value for the extinction coefficient of the peak at 660 mμ was calculated from measurements of optical densities taken for the runs described under c) and d). This was done on the assumption that the following relation was valid and applicable to any given spectrum. (See discussion, this chapter):

$$[C^+] + [3PE]_f + [X] = [3PE]_o$$

$[C^+]$ = carbonium ion conc.,

$[3PE]_f$ = free olefin conc.,

$[X]$ = conc. of unknown species absorbing at 660 mμ

$[3PE]_o$ = initial olefin conc.

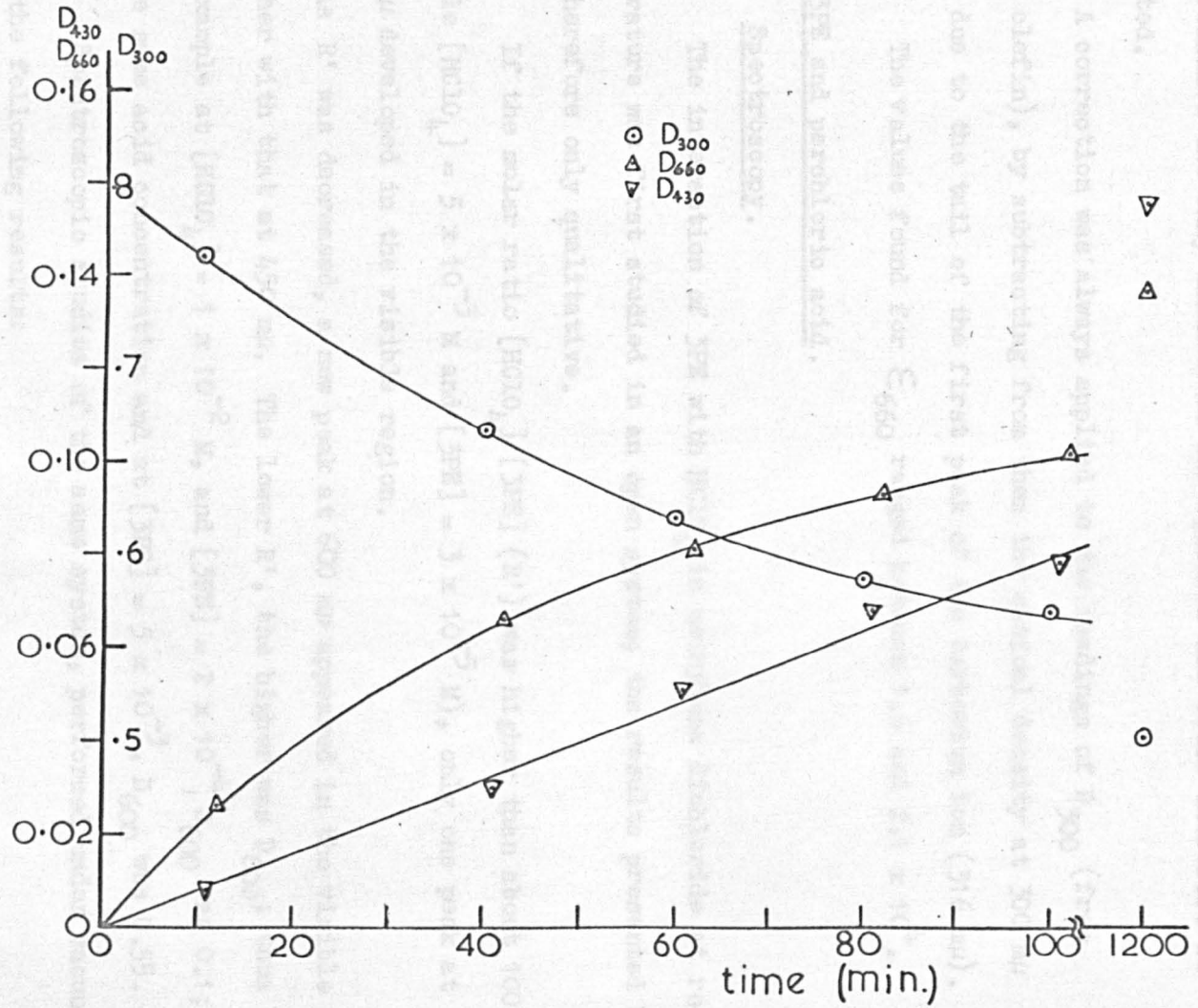

D430
D660
D300
0·16
·8
0·14
·7
0·10
·6
0·06
·5
0·02
0
D300
D660
D430
0
20
40
60
80
100
1200
time (min.)

Fig.12

Since the extinction coefficients of the olefin and of the carbonium ion peaks were known, and since I could measure the optical densities of the three peaks belonging to the corresponding species present in solution, ε_{600} remained the only unknown in the equation and could therefore be computed.

N.B. A correction was always applied to the readings of D_{300} (free olefin), by subtracting from them the optical density at 300 mμ due to the tail of the first peak of the carbonium ion (316 mμ).

The values found for ε_{660} ranged between 1.6 and 2.1 x 10^4.

2.2 3PE and perchloric acid.

2.2.1 Spectroscopy.

The interaction of 3PE with $HClO_4$ in methylene dichloride at room temperature was first studied in an open system; the results presented below are therefore only qualitative.

If the molar ratio $[HClO_4]/[3PE]$ (R') was higher than about 100 (for example $[HClO_4] = 5 \times 10^{-3}$ M and $[3PE] = 3 \times 10^{-5}$ M), only one peak at 450 mμ developed in the visible region.

As R' was decreased, a new peak at 600 mμ appeared in the visible region together with that at 450 mμ. The lower R', the higher was D_{600}; thus for example at $[HClO_4] = 1 \times 10^{-2}$ M, and $[3PE] = 2 \times 10^{-4}$, D_{600} was 0.1; at the same acid concentration and at $[3PE] = 5 \times 10^{-3}$, D_{600} was 0.55.

Spectroscopic studies of the same system, performed under vacuum gave the following results:

When R' was higher than 100 the carbonium ion peak was again the only one produced in the visible region, but λ_{max} was now 440 mμ.

Lower values of R' produced the same phenomena described for the experiments in open system, down to R' $\simeq$ 10, but the spectra changed rapidly with time. The long wavelength peak had λ_{max} = 660 mμ.

When the concentration of 3PE exceeded that of $HClO_4$, i.e. when R' was lower than 1, the situation was even more complicated because of a third peak forming in the visible region at 560 mμ; it was, however, possible to notice that whilst immediately after mixing D_{440} was much higher than D_{660} rather rapid changes occurred in the visible spectrum of the solution and within about two hours from the beginning of the reaction, D_{440} had been reduced to a very low value and D_{660} was now very high. D_{560} did not change appreciably during that time. In one case, however, when R' was 3×10^{-3} and the acid concentration only 6.1×10^{-5} M, no third peak was observed and I could follow very clearly the growth of D_{660} from 0 to 0.1 within a few hours; D_{440} remained during that time at a constant, low value ($\simeq$0.02).

2.2.2 Conductivity.

Electrical conductivity measurements were carried out with the apparatus described in Chapter One. They were restricted to a few runs in which the 3PE concentration was higher than, or equal to, the acid concentration. The solvent used was methylene dichloride and the working temperature 20°.

The specific conductivity of 3PE solutions was $3 - 4 \times 10^{-9}$ mho/cm,

that of a 4.0×10^{-2} M solution of $HClO_4$ 9×10^{-8} mho/cm. The specific conductivity of the reacting solutions ranged between 5×10^{-7} and 4×10^{-5} mho/cm, depending on the acid concentration.

When a perchloric acid phial was crushed into a 3PE solution to give $[HClO_4] = 3.1 \times 10^{-2}$ M and $[3PE] = 3.3 \times 10^{-2}$M, the conductivity went up to about 1.5×10^{-5} mho/cm within one or two minutes and then slowly rose to a constant value of 3.4×10^{-5} in three hours. During this period the solution, which had turned deep yellow-green at the mixing of the reactants, lost progressively its yellow colour to become green-black.

All the other runs, performed with different concentrations, but with the same order of magnitude for R', exhibited an analogous pattern of behaviour, i.e. a rapid increase in conductivity within the first minute or two, up to about $\frac{1}{2}$ of the final value, and thereafter a slow, but marked further increase, which tailed off in a few hours. The magnitude of K depended upon the acid concentration employed. At low concentrations (around 1×10^{-3}M for both reactants) the change in colour from greeny-yellow to pure green in the second phase of the reaction could be followed more distinctly, because of the lower intensities involved.

At the end of each run the conductivity cell was dismantled and a spectrum of the solution was taken by pouring some of it into a spectroscopic cell (and by diluting with solvent whenever required). The spectra showed a strong peak at 660 ± 3 mμ.

When high concentrations of reactants were employed, it was

occasionally noticed that a red component appeared in the colour of the reacting solution; this phenomenon was not reproducible. The final spectra of these green-reddish solutions had a second peak in the visible region at about 480 mμ.

2.3 Discussion.

In spite of several attempts at coordinating the results into a clear-cut picture, I have been unable to do so; the complexity of the systems studied has already been pointed out with respect to 2PE[3,4] and it seems to apply also to 3PE in all its unfortunate aspects.

Nevertheless, it is possible to relate the present findings to those published for 2PE, and to see which of the suggested interpretations they support best.

As far as the spectrum of 3PE in very strong acidic media is concerned, there does not seem to be any doubt about its origin. The good agreement between Gold and Tye's[1] finding and mine, together with the large body of spectroscopic data published for aromatic carbonium ions,[1,5] show that the two peaks at 316 and 430 mμ belong to the classical carbonium ion obtained by protonation of 3PE.

More problematic is the assignment of the long wavelength peak (600 - 660 mμ). The first reports about it were published in connection with the study of DPE in weakly acidic media, by Lavrushin[6] and Evans[7] et al. Following a process of elimination, Evans ascribed it to a π-complex derived from the classical carbonium ion. This interpretation was, however,

refuted by Grace and Symons[5] who showed that diphenylmethanol dissolved in weakly acidic media exhibited an analogous absorption peak and that this could not come from a π-bonding of the proton to the olefinic double bond. No alternative interpretation was offered by these authors.

The problem has recently been revived by Leftin and Hall,[7,3b] who proposed to attribute the 607 mμ peak to a cation radical formed by the interaction of the classical carbonium ion with excess of olefin (2PE). The supporting evidence they produced was based on the following observations:

a) Excess of olefin was needed in order to obtain the long wavelength peak.

b) The kinetics of formation of this coloured species in the acid mixture H_2SO_4 - CH_3COOH - $CH_2ClCOOH$ were typical of a free radical oxidation process.

c) Traces of oxidising agents (selenic acid, peroxydisulphuric acid and potassium ferricyanide) strongly accelerated the rate of increase of D_{607}.

d) A strong e.p.r. signal was obtained from a solution of 2PE and antimony pentachloride in methylene dichloride solution which gave rise to the 607 mμ peak. These authors also produced a range of values for the molar extinction coefficient of the 607 mμ peak ($\varepsilon_{607} = .5 \times 10^3 \cdot\cdot 2.2 \times 10^4$), obtained from experiments carried out in the presence of silica-alumina catalysts.

My results on the interaction of 3PE with acids show many features in support of Leftin and Hall's interpretation; these are summarised below.

a) When the protonation of the olefin is not very fast, and only then, the solutions develop the 660 mμ peak. Moreover, the lower the rate of protonation, the higher is D_{660}, and the lower the ratio $[HClO_4]/[3PE]$, the higher is D_{660}. This suggests that the reaction yielding the green species involves free 3PE.

b) At very low $[H_2SO_4]/[AcOH]$ no carbonium ions are formed and no peak at 660 mμ is observed. This seems to indicate that the reaction producing the unknown species involves the classical carbonium ions as well as free 3PE, i.e. this species cannot be produced directly from the olefin in media of low acidity.

c) The rates of formation of both classical carbonium ion and unknown species (Fig. 12) resemble those found by Leftin and Hall[3b] for 2PE.

d) The reactions promoted by perchloric acid always gave a higher proportion of green component in the spectra than the equivalent reactions in sulphuric acid. This is probably due to the oxidising power of $HClO_4$.

e) The measurements of electrical conductivity on the reacting solutions containing $HClO_4$ indicate that the relatively slow reaction which follows the fast protonation is an ion-producing one. If this slow

reaction is to be associated with the formation of the species giving rise to the 660 mμ peak, and this seems to be supported by the visual observations recorded, it follows that this unknown species must have an ionic character.

The values of ε_{660} computed in the present work for the system 3PE - H_2SO_4 - CH_3COOH (page 62) closely agree with those given by Leftin and Hall for the related species formed from 2PE.

A series of reactions involved in the formation of the cation radical has been written by Leftin and Hall[3b] on the basis of an analogous sequence proposed by Symons et al.[8] in a different context. In the present case, this could be rewritten as follows, for the system 3PE - $HClO_4$ - CH_2Cl_2:

$$Ph_2C{:}CHPh + HClO_4 \rightleftharpoons Ph_2\overset{+}{C}.CHPh + ClO_4^-$$

$$Ph_2\overset{+}{C}.CH_2Ph + Ph_2C{:}CHPh \rightleftharpoons Ph_2\overset{\cdot}{C}.CH_2Ph + [Ph_2C{:}CHPh]^{+\cdot}$$

$$Ph_2\overset{\cdot}{C}.CH_2Ph + 5\ HClO_4 \rightarrow [Ph_2C{:}CHPh]^{+\cdot} + 2\ ClO_3 + 2H_3O^+ + 3\ ClO_4^-$$

I cannot offer any explanation for the formation of the additional peak at 560 mμ obtained when an excess of 3PE was made to react with $HClO_4$, nor for the red colour noticed sometimes in the solutions used for conductivity measurements (page 65). I can however, point out that a similar phenomenon was observed by Mason[4] in the system 2PE - H_2SO_4 - CH_3COOH.

3. 4PE and acids.

3.1 4PE and perchloric acid.

The interaction of 4PE with perchloric acid in methylene dichloride was shown to produce in open experiments a lilac coloured solution. The species giving rise to this colour appeared to be extremely sensitive to moisture (much more so than conventional carbonium ions, under the same conditions), so that it was virtually impossible to conduct any preliminary study of this system. The colour formed on mixing the reactants was discharged very rapidly, even when precautions were taken to avoid absorption of moisture by the system.

3.1.1 Spectroscopy.

All runs to be described were carried out at room temperature in the usual high vacuum device, provided with 1 cm silica or pyrex cells.

As in the case of the interaction of 3PE with acids, since I have been unable to group the results of these 12 runs in a more satisfactory and rigorous way, owing to the complexity of the system, the pattern of behaviour is described below as a function of the variable $R = [HClO_4]/[4PE]$.

a) $R > 100$ (3 runs). The spectra of the reacting solutions were taken at close time intervals, and since the optical densities of the relevant peaks were decreasing with time, Gold and Tye's extrapolation[1] was used to obtain the spectra, at the time of mixing. On the assumption that these belonged to a reaction product present at a concentration equal

to the initial olefin concentration, in assuming that the interaction between acid and olefin had been fast and complete, I computed the values of the molar extinction coefficients for the whole of the extrapolated spectra. Very good agreement was obtained for the three runs, which were carried out with widely different olefin concentrations (8×10^{-6} M - 1.2×10^{-4}). Spectrum 8 shows the results obtained. The subsequent degradation reaction, due to the large excess of free perchloric acid, progressively destroyed the species responsible for spectrum 8; at R = 300 degradation was complete in about 30 min., whilst at R = 120 this lasted some 30 hours. The spectrum of the final products had only two peaks: one at λ = 260 mμ ($\varepsilon \simeq 3.5 \times 10^4$, referred to [4PE]), which persisted even after the solution had been neutralised with alcoholic ammonia; the other was at λ = 412 - 414 mμ ($\varepsilon \simeq 1 \times 10^4$) and was destroyed by moisture or by neutralisation of the solution.

b) R≃20 (2 runs, [4PE] = 1 - 2×10^{-4} M). The reactions gave rise to the same spectrum as in a), but this remained virtually unchanged (its intensity increased slightly in the first few minutes) for a few hours.

Spectrum 8 (Opposite)

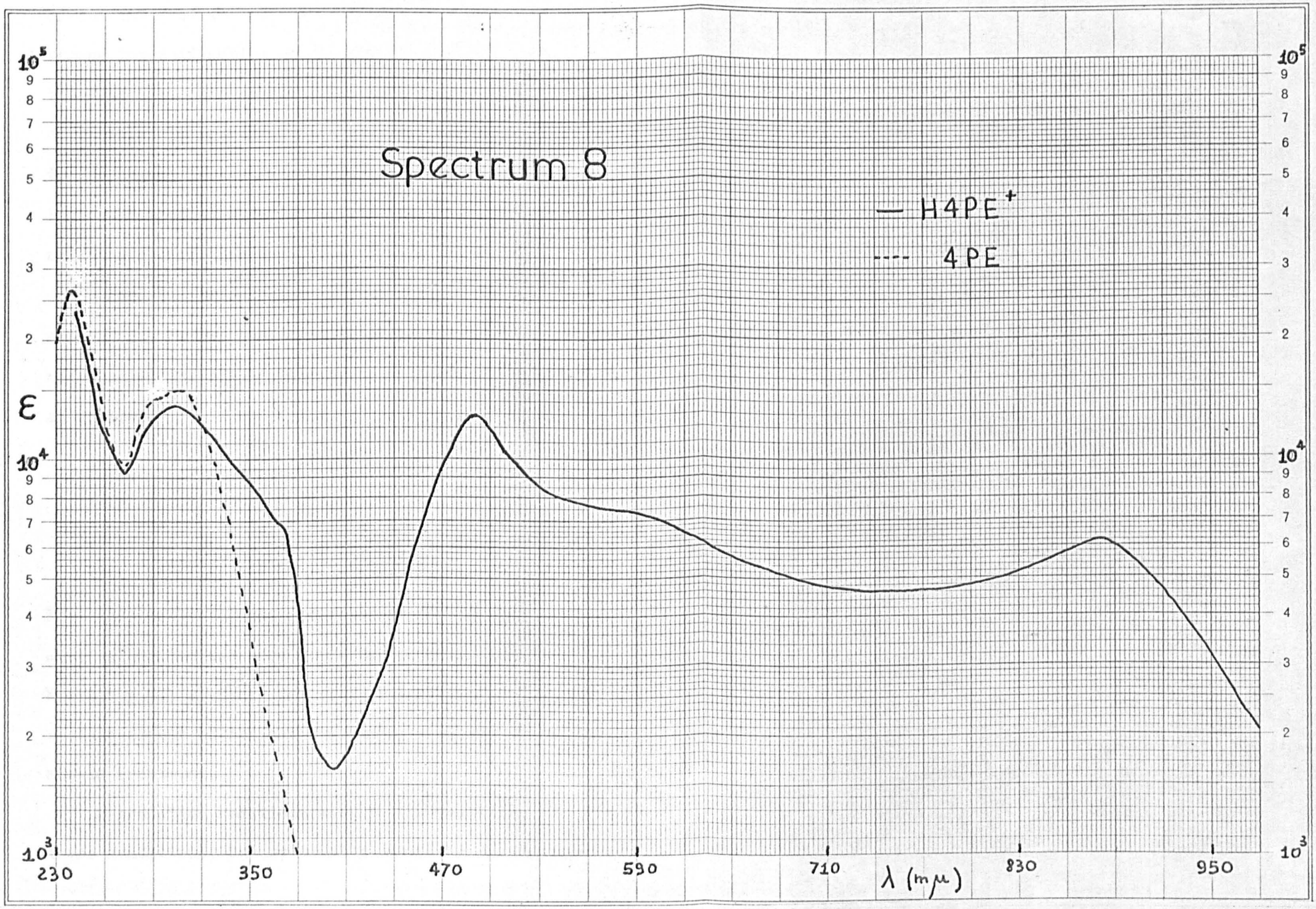
The ultraviolet and visible spectrum of the carbonium ion derived from the protonation of tetraphenylethylene, in methylene dichloride, compared with the ultraviolet spectrum of the original olefin in the same solvent.

For the olefin, see also Table 3.

For $H4PE^+$ the spectroscopic data are:

$\lambda_{max}(m\mu)$	ε_{max}
304-310	$\sim 1.35 \times 10^4$
(370)	6.9×10^3
492	1.3×10^4
(590)	7.4×10^3
880	6.2×10^3

N.B. ( ) denotes shoulder


Spectrum 8
— H4PE+
---- 4PE
ε
10^5
10^4
10^3
230
350
470
590
710
830
950
λ (mμ)

Only 20-30% of the olefin had reacted to give the coloured species. Vacuum distillation of small quantities of solvent from the cell to the lateral tube produced a strong intensification of the colour of the solution in the cell; the corresponding increase in optical density of the visible spectrum could not be ascribed solely to the change in concentration. These observations indicated that an equilibrium was set up between the reacting species and their reaction products; on the other hand electrical conductivity experiments on this system (see below) had shown that the reaction products were ionic; the equilibrium could therefore be written as follows:

$$HClO_4 + 4PE \underset{}{\overset{K}{\rightleftharpoons}} H4PE^+ + ClO_4^-$$

$$K = \frac{[H4PE^+]^2}{([HClO_4]_o - [H4PE^+])([4PE]_o - [H4PE^+])}$$

From the results of the present runs values of K were calculated and were found to be fairly consistent: $K = 2.6 \pm 0.1 \times 10^{-3}$. The scatter is possibly due to a certain amount of ion paring, which we neglected in this simple treatment.

Degradation reactions were much slower under these conditions, but eventually gave rise to the same

final spectra as those obtained in a).

c) $0.01 \leqslant R \leqslant 0.3$ (7 runs, 4PE = $1 \times 10^{-3} - 6 \times 10^{-2}$ M). These solutions had the usual spectrum; its intensity always increased with time according to rather irreproducible patterns. Step-like curves were obtained by plotting D_{491} against time, over periods of several hours. Moreover the final values of D_{491} gave values of K which did not agree with those calculated in b), the disagreement being the larger, the lower the value of R. Thus, for example, the ratio between the value of D_{491} calculated from the known value of K and the observed value ranged from 2 for R = 4, to 6 for R = 75.

In one run the perchloric acid solution was put in contact with solid olefin: the resulting mixture gave a spectrum which exhibited, apart from the usual pattern described, a new peak at 730 mμ; D_{730} did not change throughout the whole run.

N.B. Perchloric acid solutions in CH_2Cl_2 do not absorb in the interval 250-900 mμ.

3.1.2 Conductivity.

The high vacuum conductivity apparatus, described in Chapter One was used for the experiments described below; the working temperatures were

20° and 0°.

The specific conductivity of 4PE solutions was $4\text{-}8 \times 10^{-9}$ mho/cm, that of perchloric acid solutions has already been quoted (page 64). The concentrations of reactants used for these runs were an order of magnitude higher ($[HClO_4] = 5 \times 10^{-3} - 5 \times 10^{-2}$ M, $[4PE] = 5 \times 10^{-4} - 3 \times 10^{-2}$ M) than those reported in section 3.1.1.; the range of specific conductivities obtained was thus well above the background values of the starting solutions ($5 - 25 \times 10^{-6}$ mho/cm).

Runs with a large excess of $HClO_4$ (50 times or more) over the olefin reproduced well the behaviour which the system had shown in spectroscopic experiments performed under these conditions. The conductivity went to a maximum value at the time of mixing, and then started to decrease at a rate which was proportional to the excess of acid.

Successive additions of olefin to these solutions produced corresponding increases of equivalent conductivity even when the ratio R had reached values much below 1. This confirmed the hypothesis of an equilibrium being set up between the species present. The changes in conductivity did not however take place rapidly; depending on the quantity of olefin added it would take between 30 min. and several hours to reach the new equilibrium value. It was thus impossible to compute reliable values of K, since I did not know to which extent the degradation reactions had progressed during that time.

When the solutions were cooled from 20° to 0°, K_c decreased very slowly to reach a new constant value after a few hours. The phenomenon was reversible. This again indicates slow shifting of an equilibrium.

3.2 4PE and sulphuric acid.

A saturated solution of 4PE in glacial acetic acid (the olefin is sparingly soluble in this medium) was added to a large excess of sulphuric acid; a lilac colour developed on mixing, but faded away in a few seconds. The experiment was repeated a few times and always gave the same results.

3.3 4PE and trifluoroacetic acid.

In the conductivity cell under high vacuum, a phial of trifluoroacetic acid was crushed into a 4PE solution in CH_2Cl_2. The concentrations were [TFA] = 3×10^{-2} M and [4PE] = 1×10^{-3} M. No colour developed on mixing and the conductivity did not change appreciably (an increase was noticed of about 1×10^{-8} mho/cm, probably due to the conductivity of the acid). Further additions of olefin, up to [4PE] = 1×10^{-2} M did not produce any change.

A concentrated solution of 4PE in benzene was poured into a test tube containing a large excess of neat trifluoroacetic acid; the resulting solution slowly developed a lilac colour. The solution was tested in the spectrophotometer and produced a visible spectrum very similar to spectrum 8.

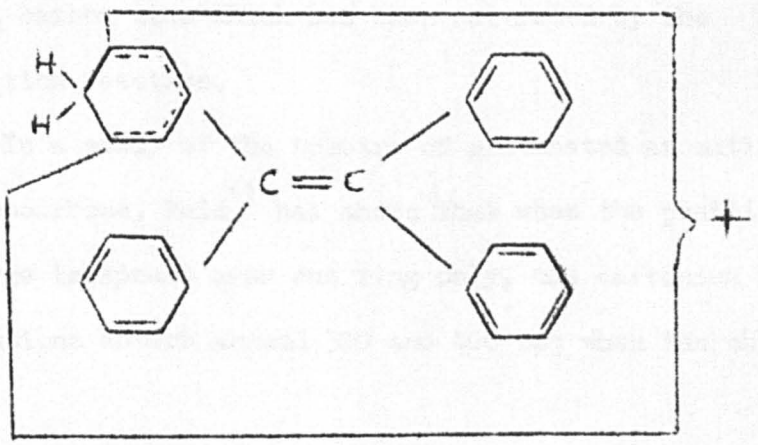
3.4 Discussion.

The interaction of 4PE with perchloric acid produces a coloured, conducting species (Spectrum 8) which is most probably a carbonium ion.

The classical carbonium ion, $CHPh_2.CPh_2^+$ would however, be expected to exhibit a spectrum very similar to those of related carbonium ions containing the chromphore $.CPh_2^+$. Gold and Tye[1] have discussed at length the spectral characteristics of this group. Spectrum 8 does not show any similarity with those, say, of the 1,1-diphenylethyl- or 1,12-triphenylethyl carbonium ions. It is likely that protonation of the olefinic double bond is sterically hindered by the four phenyl groups, which are all rotated out of its plane.[9] The acid solution contains in fact $HClO_4$ covalent molecules (or, more probably, aggregates of these molecules, see Chapter Four) which are rather bulky and which could therefore not reach the electronic cloud around the double bond.

This strong steric effect has already been noticed in 4PE, which was reported not to add bromine at the olefinic double bond.[10]

The attack of perchloric acid on this olefin must therefore take place at another, more exposed, site in the molecule; the most likely sites are obviously the four equivalent <u>para</u> positions on the benzene rings. It follows that under the present conditions the protonation of 4PE produces a carbonium ion, the structure of which can be schematically represented as in II.



II

The features of Spectrum 8 seem to support this particular structure as discussed below.

a) In the u.v. part of the spectrum the conjugation band of 4PE at 308 mμ persists and only suffers a minor hypochromic shift. This indicates that the protonation reaction does not affect appreciably the extent to which the phenyl groups are conjugated with and through the olefinic double bond. If the proton addition had taken place at this double bond, the conjugation would naturally have been completely destroyed, as happens when the other phenylated olefins react with strong acids.[1]

b) The lower energy section of Spectrum 8 is more difficult to interpret. The carbonium ion II has been depicted by conventional[1] but rather vague notations, as far as charge distribution is concerned. I have assumed that the positive charge is spread at least to a certain extent over the whole of the molecule, except for the para carbon atom which has been saturated by the addition reaction.

In a study of the spectra of protonated aromatic hydrocarbons, Reid[11] has shown that when the positive charge is spread over one ring only, the carbonium ion solutions absorb around 300 and 400 mμ; when the charge

is shared by two rings, the peaks are shifted to 400 and 500 mμ respectively. Although the carbonium ion II does not strictly belong to the class of ions studied by this author, it seems likely that Reid's observations should apply to it, as to any cationic system involving conjugated phenyl groups.

The present spectrum with its two main peaks at 491 and 880 mμ, can be accounted for, on the basis of what has just been discussed, by considering these two bands as the result of a strong bathochromic shift compared to the "normal protonated ring absorption" due to a large degree of spreading of the positive charge over the four phenyl groups and over the olefinic double bond, despite the non-planarity of the 4PE molecule. The very existence of this unusual ion is probably only made possible by the decrease in the energy of the system by charge dissipation.

Free perchloric acid seems to be needed to stabilise the carbonium ion II; this is suggested by the findings reported for runs involving an excess of 4PE (see point c., page 72), in which the protonation proceeded to a lesser extent than in the corresponding runs with excess of acid.

The behaviour of the system 4PE - H_2SO_4 - CH_3COOH is probably to be ascribed to the occurrence of the following phenomena: 4PE is slightly

soluble in acetic acid, but is insoluble in sulphuric acid;[1] when the acetic acid solution of this olefin is poured into an excess of sulphuric acid, 4PE is precipitated, but not instantaneously. The metastable solution of 4PE in sulphuric acid produces some carbonium ions II, which, however, are very short lived.

The experiments with trifluoroacetic acid indicate that a medium of very high acidity is needed for the carbonium ions II to be formed; this is compatible with the requirements of protonation on the ring in general.[11]

Evans and co-workers have reported that 4PE interacts with trichloroacetic acid in benzene and nitrobenzene in an open system to give coloured solutions. The absorption maxima occurred at 425, 445, and 680 mμ. No indication was given of the concentrations used.

I have repeated these experiments using various 4PE and acid concentrations, but I did not succeed in obtaining any colour formation.

Apart from the run in which a green colour was obtained when the $HClO_4$ solution came in contact with solid 4PE, and apart from the brownish colour of the deteriorated solutions (from runs with excess of perchloric acid), I have never obtained from this system any visible spectrum other than that reported (Spectrum 8).

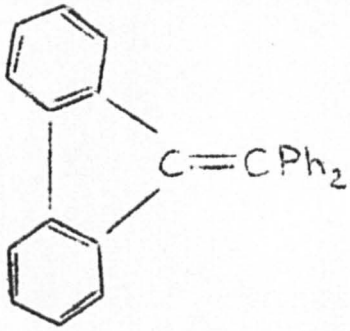
I wish to thank Professor M.C.R. Symons for helpful comments on this part of my work.

4. Conclusions and suggestions for further work.

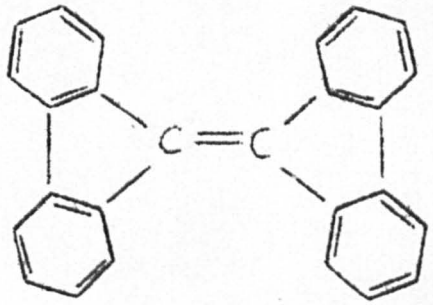
The work reported above has proved to be insufficient for a definitive

solution of all the problems encountered. However, a more systematic attack on these questions would have required a much larger amount of work and it was not my intention at the time to devote a major effort to the solution of problems which had no directly bearing on the original aims of this research.

The interaction of 4PE with strong acids produced a most interesting new carbonium ion, the first of its kind. It is my intention to ascertain its structure by the use of NMR spectroscopy. Moreover it would be interesting to study the characteristics of the proton adducts of compounds similar in structure to 4PE (such as III and IV), in order to widen the exploration of this new class of carbonium ions.



III



IV

The most important piece of information which I expected to obtain from the present investigation, namely a quantitative correlation between spectroscopic and conductimetric data on carbonium ion solutions, failed to materialise because of ill-controlled side reactions.

I decided therefore to refrain from concentrating on these difficulties and to switch instead directly to the study of a polymerisable olefin, in the hope of obtaining more reliable results.

References to Chapter Three

1. Gold and Tye, J.Chem.Soc., 1952, 2172.

2. Kohn, J.Phys.Chem., 1962, 66, 1185.

3. See for example, a) Evans, Jones and Thomas, J.Chem.Soc., 1957, 104.
   b) Leftin and Hall, J.Phys.Chem., 1962, 66, 1457.

4. Mason, M.Sc. Thesis, Durham, 1963.

5. Grace and Symons, J.Chem.Soc., 1959, 958.

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CHAPTER FOUR

THE INTERACTION OF POLYMERISABLE OLEFINS WITH ACIDS AND LEWIS ACIDS

PART I : STYRENE

1. Introduction.

The polymerisation of styrene catalysed by acids and Lewis acids has been widely studied and Mathieson[1] has recently reviewed this subject very thoroughly. The chemical interpretation of the reactions involved in these systems has invariably been based on the assumption that the chain carriers produced in the initiation reaction are carbonium ions, i.e. 1-phenylethyl, and subsequently polystyryl, ions. The literature, however, does not provide any irrefutable proof for this interpretation, although a number of attempts directed towards this aim has been made; I shall discuss these attempts together with my own results later in this Chapter.

My choice of perchloric acid as catalyst and protonating agent has already been discussed.

2. The 1-phenylethyl and polystyryl ions.

2.1 Results.

The protonation of styrene by perchloric acid was studied at room temperature (18-23°) in methylene dichloride, by means of the customary high vacuum device attached to a 1 cm silica cell which has been described.

The best working conditions were attained with an approximately hundredfold excess of acid with respect to the styrene concentration;

more acid made side reactions too important, less acid tended to slow down the protonation reaction, so that a mixture of 1-phenylethyl and polystyryl ions was obtained, because of partial oligomerisation of the styrene.

The absorption maximum in the visible spectrum due to the 1-phenylethyl ion was located in a few preliminary runs and was found to be at 427 ± 1 mμ. It was noticed that D_{427} increased during the first few minutes following the mixing of the reactants, and I therefore decided to measure the rate of protonation by scanning at this wavelength against time.

Four runs were conducted for this purpose; the reaction traces were analysed and gave good first order plots up to 90-95% conversion, as shown in Fig. 13. A plot of the logarithm of the slope of the first order plot against the logarithm of the acid concentration (Fig. 14) gave a straight line with slope 0.24 ± 0.02 and intercept -1.63 ± 0.02.

A plot of the final D_{427} against the styrene concentration (Fig. 15) gave a reasonably good straight line passing through the origin; its slope, calculated by the least squares method, was $(3.86 \pm 0.07) \times 10^{-3}$ l m^{-1} cm^{-1}.

Full spectra of the solutions were frequently scanned at the end of the protonation reaction. Under the conditions described side reactions occurred, which were, however, fairly slow compared with the protonation itself. These side reactions produced a strong increase in absorption around 250 mμ with parallel (but less strong) decrease of D_{427}. In order to obtain the full spectrum of the 1-phenylethyl ion, the original values of D at several wavelengths were derived by applying the zero time extrapolation technique suggested by Gold and Tye.[2] Good Lambert-Beer plots were obtained

by plotting the extrapolated D_λ values at a given wavelength, against the styrene concentration. It was thus possible to trace the spectrum of the 1-phenylethyl ion in the region 250-800 mμ (spectrum 9); the only peak in the u.v. had $\lambda_{max} = 309 \pm 0.5$ mμ and $\varepsilon_{309} = 1.66 \pm 0.05 \times 10^3$. The data relevant to the reactions just described are summarised in Table 5.

As already mentioned in Chapter Two, three runs were carried out in the same conditions as those just described, but using 1-phenylethanol instead of styrene. From these rates of protonation were obtained, which were similar to those obtained with styrene, although the scanning was started too late for a good kinetic analysis to be performed on the reaction curves. The spectra exhibited two peaks at 309.5 ± 0.5 mμ and at 429 ± 2 mμ ($\varepsilon_{429} = (3.8 \pm 0.1) \times 10^3$), in excellent agreement with those obtained for styrene.

The linear dimer of styrene was then protonated under the same conditions (three runs). Even in the presence of a large excess of acid, the protonation reaction was always accompanied by the cyclisation of 1,3-diphenylbutene-1 to 1-phenyl 3-methylindane,[3] as indicated by the formation of peaks at 267 and 274 mμ. The computation of molar extinction coefficients as well as of reaction rates was made impossible by this complication. The spectrum of the carbonium ions had two peaks at 308 ± 0.5 mμ and at 424 ± 1 mμ respectively. These were certainly due to the species $CH_3.CHPh.CH_2.CHPh^+$, since the pure cyclic dimer does not interact with perchloric acid under the present conditions.

The spectrum of the 1-phenylethyl ion was also studied in

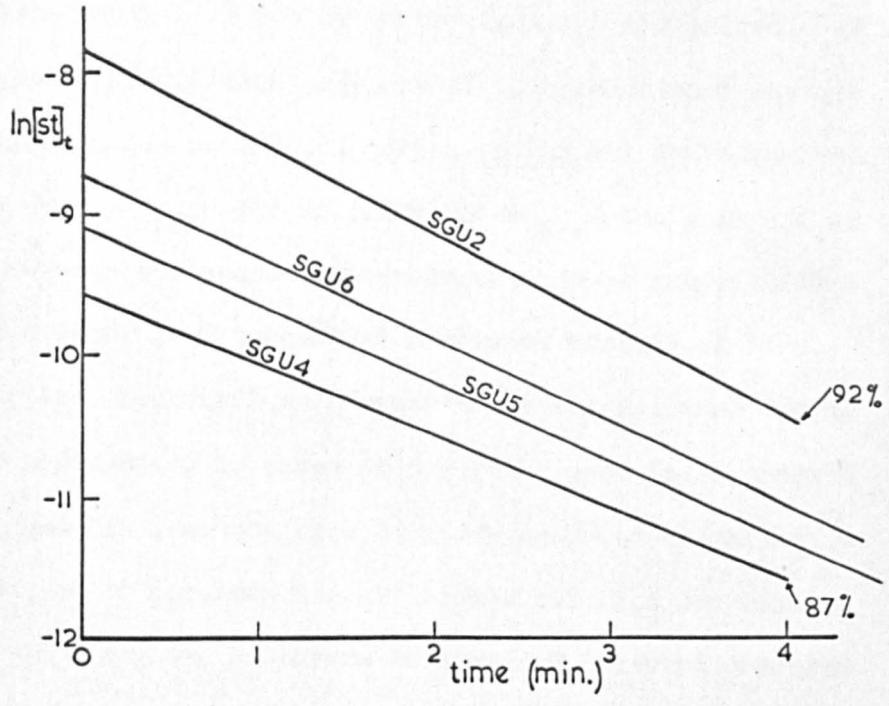

-8
ln[st]t
-9
-10
-11
-12
SGU2
SGU6
SGU4
SGU5
92%
87%
0
1
2
3
4
time (min.)

Fig.13

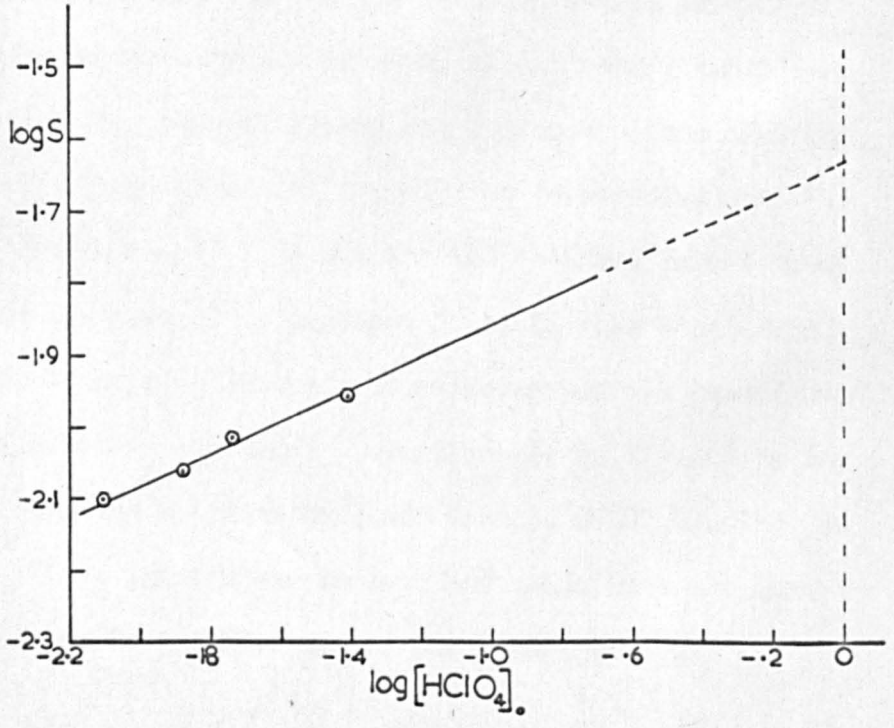

-1·5
log S
-1·7
-1·9
-2·1
-2·3
-2·2
-1·8
-1·4
-1·0
-·6
-·2
0
log [HClO4]o

Fig.14

Table 5

Data on the protonation of styrene

Run	$[HClO_4]_o$ (10^2M)	$[st]_o$ (10^4M)	S* ($10^2 sec^{-1}$)	Max. D_{427}
SGU2	3.95	3.87	1.10	1.50
SGU3	2.48	2.24	-	0.92
SGU4	0.780	0.723	0.80	0.21**
SGU5	1.34	1.36	0.87	0.49
SGU6	1.81	1.65	0.97	0.65

*Slope of the first order plot

**Traces of oligomers were formed during this experiment: the maximum value of D_{427} is therefore lower than expected (see Fig. 15).

Fig. 13 (opposite) First order plots for the reactions studied (see Table above)

Fig. 14 (opposite) The order in perchloric acid for the reactions.

Fig. 15 (next page) The Lambert-Beer plot for the 1-phenylethyl carbonium ion.

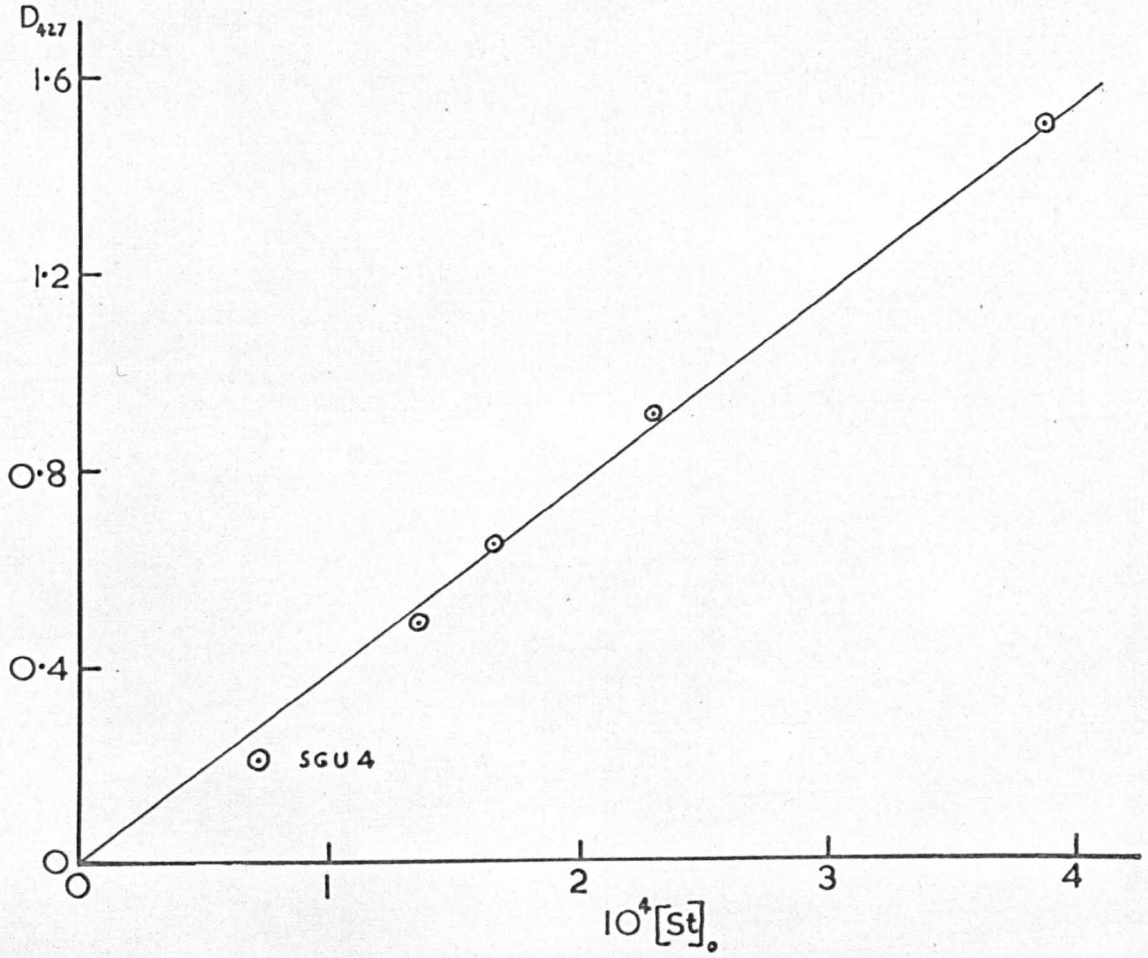
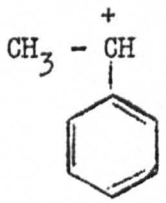


Fig.15

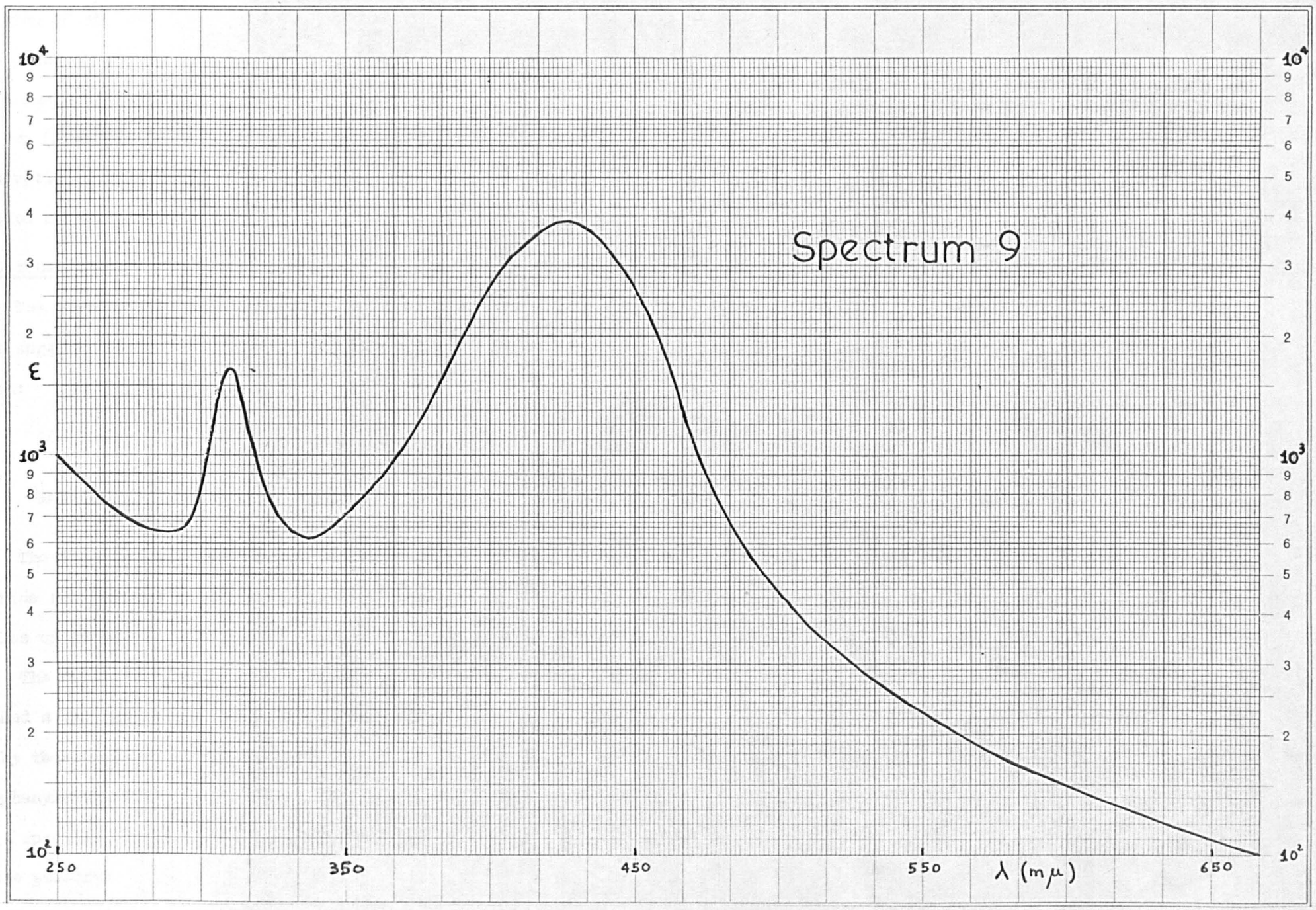
Spectrum 9 (Opposite)

The ultraviolet and visible spectrum of the 1-phenylethyl carbonium ion in methylene dichloride.



$\lambda_{max}(m\mu)$	$10^{-3}\varepsilon$
309 ± 0.5	1.66 ± 0.05
427 ± 1	3.86 ± 0.07

See also Table 6


Spectrum 9
ε
10^4
9
8
7
6
5
4
3
2
10^3
9
8
7
6
5
4
3
2
10^2
250
350
450
550
λ (mμ)
650

1,2-dichloroethane (2 runs), by the procedure described above. The protonation of styrene yieldsdat first the 1-phenylethyl ion, the spectrum had two peaks at 309 ± 1 mμ and at 427 ± 1 mμ ($\varepsilon \approx 4 \times 10^3$), but this changed within a few minutes to give an additional peak in the visible region at 396 ± 1 mμ ($\varepsilon \approx 4 \times 10^3$). The subsequent degradation reactions reduced the absorption in the visible region and increased correspondingly the absorption around 250 mμ, as in the reactions carried out in CH_2Cl_2.

2.2 Discussion.

The results obtained from the kinetics of the protonation of styrene suggest that the reaction proceeds according to the following equation:

$$1/4(HClO_4)_4 + CH_2{:}CHPh \xrightarrow{k_i} CH_3.CHPh^+ + ClO_4^-$$

$$\text{Rate} = k_i\,[HClO_4]^{1/4}\,[\text{Styrene}] \qquad k_i = (2.35 \pm 0.1) \times 10^2\ l^{0.25}_{m}\,^{-0.25}_{sec}\,^{-1}$$

The 1/4 power in acid indicates that this is associated in methylene dichloride solutions into molecular aggregates containing on average 4 molecules of acid.

The first report on the spectrum of the 1-phenylethyl ion was published a few years ago by Inoue and Mima;[4] only the absorption maxima were given by these authors who dissolved alternatively liquid and gaseous styrene and 1-phenylethanol in 95% sulphuric acid in order to produce the carbonium ion. A spectrum of the protonated styrene linear dimer in the same medium was also published. From direct readings on their spectra (not all the data

are given in the text), I obtained the values for the different λ_{max}'s (Table 6). Inoue and Mima assigned the peak at 450 mμ to the 1-phenylethyl ion and that at 416 mμ to the distyryl ion. This conclusion seemed to me rather surprising since I thought, on the basis of general considerations, that only a very small hypsochromic shift would be produced by substituting a hydrogen atom in the methyl group next to the chromophore by a second monomer unit.

Grace and Symons[5] reported more recently on the spectrum of the 1-phenylethyl ion obtained under conditions similar to those employed by Inoue and Mima. The figures obtained by these authors are also given in Table 6.

A more thorough investigation of the same system was provided by Jordan and Treloar[6] who studied the changes in spectra occurring with time when wtyrene or 1-phenylethanol were dissclved in concentrated sulphuric acid. By the usual extrapolation technique,[2] they obtained the full spectrum at the time of mixing (Table 6). The secondary reactions tended to destroy the carbonium ions and to produce species absorbing strongly around 270 mμ. These authors also studied the spectra of polymerising (or polymerised?) solutions and gave figures for the absorption maxima of the polystyryl ion in different solvents (Table 6); again a shift of 25 - 30 mμ was reported to take place when passing from the monomer to the polymer ion.

Finally, Reilly[7] has reported the visible spectrum of the polystyryl ion in 1,2-dichloroethane (Table 6).

A comparison of my results (which are also shown in Table 6 to help

Table 6

Spectroscopic data on the styryl and polystyryl ions

Compound	Solvent	Proton Donor	Alledged carbonium ion	λ_{max} (ε_{max}) (mμ)	Ref.
Styrene (gas)	H_2SO_4	H_2SO_4	$CH_3.CHPh^+$	316 (-), 450 (-)	4
1-phenyl-ethanol	"	"	"	450 (-)	"
1,3-diphenyl-butene-1	"	"	$CH_3.CHPh.CH_2.CHPh^+$	306 (-), 416 (-)	"
styrene	"	"	$CH_3.CHPh^+$	435 ($\approx 10^4$)	5
1-phenyl-ethanol	"	"	"	435 ($\approx 10^4$)	"
styrene	"	"	"	270 (1340), 308 (1310), 430 (1020)	6
1-phenyl-ethanol	"	"	"	270 (1770), 305 (1930), 430 (1020)	"
1-phenylethylchloride	$(CH_2Cl)_2$	$SnCl_4$	"	440 (-)	"
"	CCl_4	$AlCl_3$	"	445 (-)	"
-	$(CH_2Cl)_2$	$SnCl_4$	$CH_3.CHPh.(CH_2.CHPh)_n.CH_2.CHPh^+$	410 (-)	"
-	CCl_4	$AlCl_3$	"	420 (-)	"
	$(CH_2Cl)_2$	$HClO_4$	"	416 (160)	7
styrene	CH_2Cl_2	$HClO_4$	$CH_3.CHPh^+$	309 (1660), 427 (3860)	present work
1-phenyl-ethanol	"	"	"	309.5(-), 429 (3800)	"
styrene	$(CH_2Cl)_2$	"	"	309 (-), 427 (-)	"
1,3-diphenyl-	CH_2Cl_2	"	$CH_3.CHPh.CH_2.CHPh^+$	308 (-), 424 (-)	"

comparison) with those previously published suggest the following considerations.

a) The spectrum of the styryl ion obtained under the present conditions does not exhibit any absorbtion maximum between 250 and 300 mμ in contrast to the peak at 270 mμ found by Jordan and Treloar;[6] on the other hand, the changes which these spectra undergo with time are very similar in both instances and they consist of a strong increase in absorbtion in the region 250-270 mμ. This indicates that, probably because of the relatively slow scanning possibilities of the instrument used by Jordan and Treloar (UNICAM manual SP 500), and a peculiarly fast increase in absorbtion at 270 mμ soon after the mixing, these authors have mistaken a peak due to species originating from side reactions for one belonging to the carbonium ion.

b) The molar extinction coefficient for the peak at 427 mμ (my results in CH_2Cl_2) is roughly four times higher than that of the peak at 430 mμ in sulphuric acid;[6] this can hardly be attributed to a simple solvent effect. It seems more likely that because of the side reaction giving the anomalous behaviour discussed under a), less styrene is in fact available for protonation under the conditions used by Jordan and Treloar. This side reaction seems to be either sulphonation of the styrene, in spite of the special precautions taken by the authors,[6] or partial polymerisation of the olefin, with consequent decrease in the number of double bonds available. This second hypothesis is corroborated by the fact that polystyrenes absorb at 260 mμ.

c) The present spectrum of the 1-phenylethyl ion agrees in its pattern with the spectra of homologous carbonium ions (such as 1,1-diphenylethyl; 1,1,2-triphenylethyl carbonium ions[2]) in so far as they all exhibit two peaks, one in the u.v. around 300 mμ and the other in the visible at 430-440 mμ, with ε_{300} roughly $\frac{1}{2}$ of $\varepsilon_{430-440}$.

d) The spectra of the styryl ion in methylene dichloride and in 1,2-dichloroethane are virtually equivalent; I have not been able to ascertain the origin of the peak at 396 mμ appearing in the latter solvent after the protonation reaction. Since this peak was the only one exhibited by visible spectra of polymerised solutions in the same solvent (see section 3.1.2.), it seems likely that its origin is to be related with some rearrangement of long chain carbonium ions to form tertiary cations. It is possible that, owing to formation of oligomers during the protonation, the ions could rearrange according to the following reaction:

$$CH_3.CHPh.CH_2.\overset{+}{C}HPh \rightarrow CH_3.\overset{+}{C}Ph.CH_2.CH_2Ph$$

It is known that the dimethylphenylcarbonium ion absorbs at 390 mμ in sulphuric acid[5] or at 395 mμ according to another author.[8] This supports my interpretation, since the tertiary carbonium ion depicted above would have virtually the same chromophore as the dimethylphenyl-carbonium ion. I cannot explain at the moment why this rearrangement should take place in one solvent and not in the other (methylene dichloride), but it seems likely that the protonation was faster in

CH_2Cl_2 and thus oligomerisation avoided. This point will, however, be considered further, after the illustration of my results on polymerising systems involving styrene and perchloric acid. The protonation of α-methylstyrene in an open system, performed with a large excess of perchloric acid with respect to the olefin, in methylene dichloride gave a peak at 394 ± 2 mμ (two runs).

e) As expected, the spectrum of the distyryl ion closely resembles that of the monomer ion; only a minor hypsochromic shift, amounting to about 3 mμ for the longer wavelength peak, is produced by the substitution of one hydrogen of the methyl group by a monomer unit. These findings are in strong disagreement with the observations of the cited authors. However, it seems very likely that the spectra they attributed to simple secondary dimer (or polymer) ions were in fact due to tertiary ions of the kind illustrated in d), or to some other isomeric structure. The peaks reported for these spectra were always very broad in contrast to the fairly sharp peak I obtained from my experiments. This again suggests that a mixture of different ionic species was present in the solutions studied by these authors. These points will receive more attention in the following sections of this Chapter.

f) Although I was unable to obtain reliable values for the molar extinction coefficients of the distyryl ion, it is reasonable to assume that these should not differ much from those of the

1-phenylethyl ion; since the chromophore is not sensibly altered by the substitution as far as the position of the maxima is concerned, a variation in its absorption power would hardly be expected.

In conclusion, for all purposes related to the present work, it seemed safe to assume that the polymer ion would absorb virtually in the same positions as the dimer ion (this point was proved true, see Section 3.2.1.) and that the extinction coefficients of the two maxima would be virtually equal to those of the corresponding maxima exhibited by the monomer ion.

3. The polymerisation catalysed by perchloric acid

Knowledge of the spectral characteristics of the 1-phenylethyl and distyryl ions permitted me to move forward in this work and to start the search for ions in the polymerising solutions.

I started therefore to carry out spectroscopic experiments in order to verify directly Pepper and Reilly's theory on the fast and complete protonation of styrene by perchloric acid.[7] Since my observations were totally against this theory, and since at first I used methylene dichloride as solvent instead of 1,2-dichloroethane,[7] I thought it would be wise to check upon the actual polymerisation kinetics of my system before drawing any definite conclusions; having done that, I repeated some of the experiments previously carried out in the spectroscopic device and measured the conductivities of the reacting solutions.

3.1 Results.

For reasons of consistency, I have grouped all the results obtained

from the three families of experiments in one section.

Whenever possible, results from spectroscopic and conductimetric experiments are directly compared to show the extent to which they agree.

Captions and notes referring to a given Figure are to be found on the page opposite to it.

Before proceeding to a discussion of the results obtained, I am going to outline briefly the general features of the runs conducted with each technique, following the chronological and logical order.

More results are to be found below; they refer to runs conducted in solvents other than methylene dichloride.

N.B. Although the results reported refer only to high vacuum experiments, the following account refers also to a number of experiments in open systems (conductivity and spectroscopy) carried out at the beginning of this work.

3.2 Spectroscopy.

In order to follow the changes in carbonium ion concentration, after the mixing of the reactants, it was decided to scan at 424 mμ against time; the choice of this particular wavelength was dictated by the fact that in the spectrum of the distyryl ion the most prominent peak is that at 424 mμ (Table 6). Also, the presence of high styrene concentrations made it frequently impossible to obtain any u.v. spectrum at all; except for a few experiments, in which silica cells were used because I could record u.v. and visible spectra of the reacting solutions, the major part of this work was conducted in the usual spectroscopic device provided with 1 cm pyrex cells.

All the runs to be described were carried out at room temperature (18-23°).

3.2.1 The reactions in methylene dichloride.

Provided that the ratio $[st]_o/[HClO_4]_o$ was higher than about 4, D_{424} did not exceed 0.0087 (experimental error for D = 0.000) after the mixing of the reactants. This indicated that if styryl or polystyryl ions were produced at all, their concentration was always lower than about 3×10^{-6}M, even at acid concentrations as high as 2×10^{-3}M.

In several runs the whole of the visible spectrum was repeatedly scanned soon after the mixing, but no peak could be detected during this first part of the reactions.

After this period of complete optical transparency (induction period, t') which was the longer, the higher the styrene concentration (at fixed $[HClO_4]_o$) and the shorter, the higher the acid concentration (at fixed $[st]_o$), polystyryl ions began to appear and the solutions exhibited an increasingly strong absorption at 424 mμ.

Towards or after the end of this ionic growth, the spectra of the reacting solutions slowly developed a rather broad peak around 450 mμ, while D_{424} decreased correspondingly. The rate of appearance of this second peak was roughly proportional to the initial styrene concentration for a given $[HClO_4]_o$. This third reaction virtually eliminated the peak at 424 mμ.

A fourth phase in the reactions produced, hours after the beginning, a slow build-up of a twin band with maxima at 390 and 410 mμ, whilst D_{450} slowly decreased to a low constant value.

On opening the device to the atmosphere, and treating the solutions with a drop of ethanol, the peak at 450 mμ disappeared completely, but the twin peaks at 390 and 410 mμ remained unchanged.

N.B. A rather fast phenomenon was observed in these reactions, but I only succeeded in recording it once: immediately after the induction period, but before the formation of the golden-yellow colour (424 mμ) due to the polystyryl ions, the solution turned pinkish-red for a very short time. This colour corresponded to a peak at 510 mμ, which had a very short life. It was not present during the induction period, it was produced just at the end of it, and it vanished again soon after. The lifetime of this peak ranged between 5 and 30 seconds.

A typical example of the general behaviour of these reacting solutions, is shown in Fig. 16, where spectra at different times for a given run have been put in chronological order to illustrate the transformations taking place. Also, the list of absorption maxima, opposite to Fig. 16, gives a key for the origin of these peaks; it is offered here before the actual interpretation of the results in order to facilitate the understanding of this rather complicated behaviour.

A second addition of styrene to the reaction mixture at any time after the formation of ions, caused complete discoloration; the peaks at 424 mμ and 450 mμ disappeared; in a run which had been going for several hours, only the twin peaks at 390 mμ and 410 mμ were left. After a second induction period, the solution started absorbing again at 424 mμ and

A list of the visible absorption maxima and their origin, for the systems $HClO_4$ - styrene - CH_2Cl_2 and $HClO_4$ - styrene - $(CH_2Cl)_2$.

λ_{max} ($m\mu$)	Origin
395	Tertiary polystyryl ions
390 and 410	Polyunsaturated "dead" polystyrene
424	Secondary polystyryl ions
450-480	Allylic ions formed by abstraction of a hydride ion from an unsaturated polystyrene molecule.
510	Transitory species formed at the end of the induction period, before the polystyryl ions appear.

Fig. 16 (opposite)

A typical sequence of visible spectra for a spectroscopic run.

a: at the end of the ion formation (only polystyryl ions)

b: some 10 - 20 minutes later. (mixture of polystyryl and allylic ions)

c: about 1 hour later (more allylic ions)

d: a few hours later (dienic polymer molecules + allylic ions)

e: 20 - 30 hours later (more dienic polymer molecules and less allylic ions)

f: same as e) after addition of a few drops of ethanol (only dienic polymer molecules)

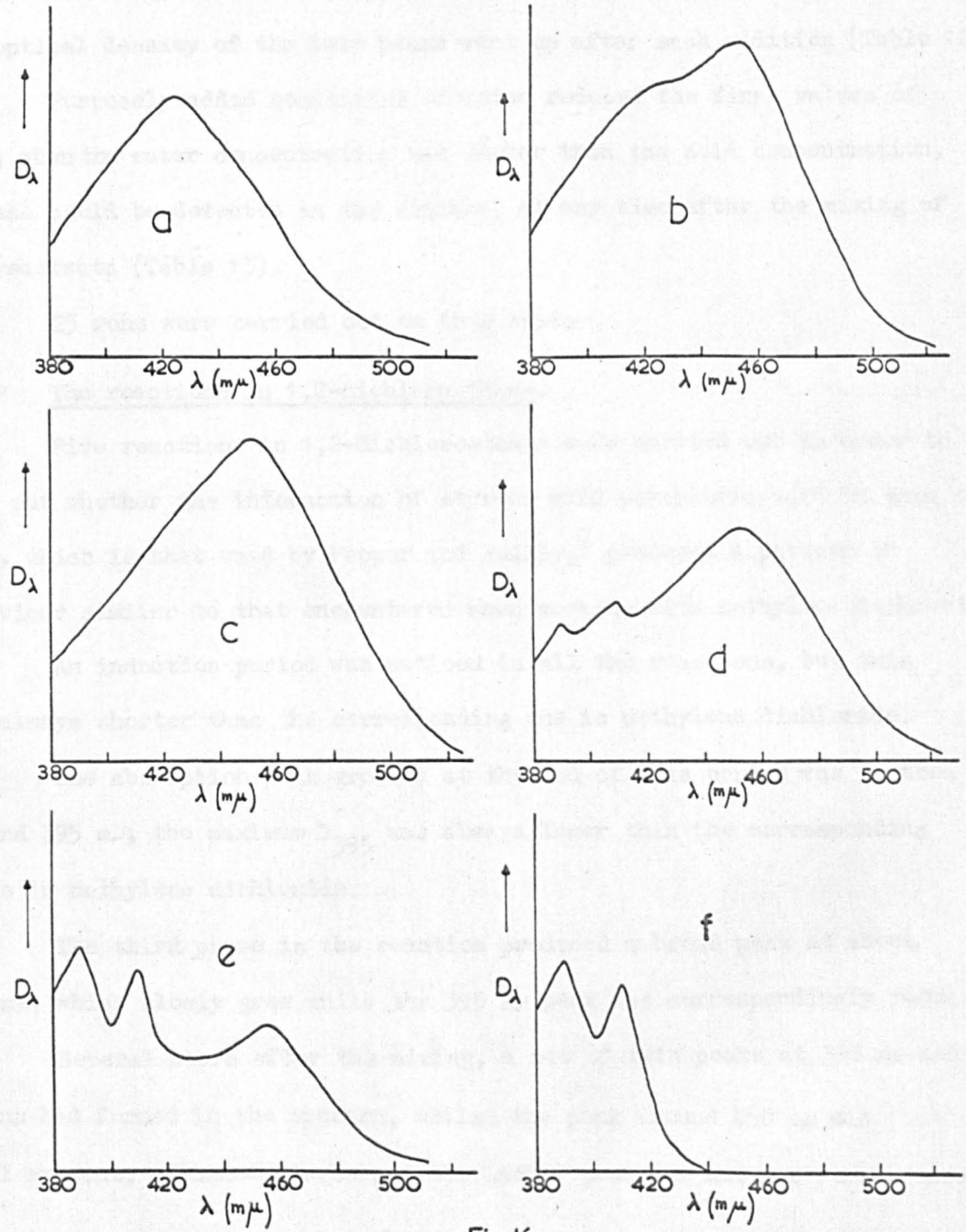


Fig. 16

subsequently at about 460 mμ. The final D_{424} and D_{460} were higher than those at the end of the first reaction. A third addition brought about the same series of phenomena. The optical density of the twin peaks went up after each addition (Table 14).

Purposely added quantities of water reduced the final values of D_{424}; when the water concentration was higher than the acid concentration, no peak could be detected in the visible, at any time after the mixing of the reactants (Table 13).

25 runs were carried out on this system.

3.2.2 The reactions in 1,2-dichloroethane.

Five reactions in 1,2-dichloroethane were carried out in order to find out whether the interaction of styrene with perchloric acid in this solvent, which is that used by Pepper and Reilly,[7] produced a pattern of behaviour similar to that encountered when working with methylene dichloride.

An induction period was noticed in all the reactions, but this was always shorter than the corresponding one in methylene dichloride.

The absorption peak growing at the end of this period was centred around 395 mμ; the maximum D_{395} was always lower than the corresponding value in methylene dichloride.

The third phase in the reaction produced a broad peak at about 450 mμ, which slowly grew while the 395 mμ peak was correspondingly reduced.

Several hours after the mixing, a set of twin peaks at 390 mμ and 410 mμ had formed in the spectra, whilst the peak around 450 mμ was still present. Ethanol discharged the latter peak but not the former ones.

In conclusion, the behaviour of this system closely resembled that of the previous one; the only remarkable qualitative difference was the formation of a peak at 395 mμ as opposed to one at 424 mμ in the experiments with methylene dichloride.

3.2.3 The reactions in nitroalkanes.

When a phial containing perchloric acid solution in methylene dichloride was crushed into a large excess of a styrene solution in nitromethane, a vigorous reaction (polymerisation) took place immediately. The polymer was precipitated in the form of a whitish gel, and no spectra could therefore be taken; the solution remained colourless throughout these reactions. Two runs were carried out under these conditions; the concentrations used were $[HClO_4]_o = 1.0 \times 10^{-3}$ M and $[st]_o = 0.41$ M in both, but water was purposely added to one of the solutions to give a ratio $[H_2O]/[HClO_4]_o$ of about 3. In both runs, as already mentioned, the polymerisation was very fast and gave 100% yield. No difference could be noticed between the two experiments.

The $\overline{DP}$ of the polymers obtained was 4 in both experiments.

When styrene was polymerised under the same conditions, but in nitroethane, no ions could be detected during or after the polymerisation, although the polymer is soluble in this solvent.

Two reactions were carried out under conditions similar to those used by Reilly,[7] viz. in a solvent mixture containing 40 vol. % of nitroethane, 55 vol. % of ethylene dichloride, and 5 vol. % of styrene. The polymerisation was relatively slow, (25% conversion in 50 minutes at $[HClO_4]_o = 4.8 \times 10^{-4}$ M)

but went to completion; no styryl ions could be detected spectroscopically during or after the polymerisation.

3.3 Polymerisation kinetics.

The rate of polymerisation was followed only in methylene dichloride. Calorimetric experiments at 19°, 0° and -19° gave kinetic features in excellent agreement with those reported by Pepper and Reilly.[7] The reactions were found to be of first order overall (Fig. 18), and the slope of the first order plot was directly proportional to the acid concentration at any given temperature (Fig. 21, 22, 23).

Close observation of the colour of the reacting solutions revealed that while the polymerisations proceeded, the solutions remained colourless, but towards the end, i.e. when the reaction curve became virtually parallel to the time axis, they turned first pinkish-red for a very short time, then progressively deeper golden-yellow (see Fig. 17).

When the acid concentration was high ($> 7 \times 10^{-3}$ M), as required in runs at the lowest temperature in order to obtain reaction rates reliably measurable by the present calorimetric technique, the colour appeared before the polymerisation was over. At the time corresponding to the colour formation the reaction curve registered a sudden strong increase in rate of heat production, which lasted only a few seconds; after this sudden rise in temperature the reaction was virtually over (the trace was now parallel to the time axis). This phenomenon is shown in Fig. 19.

Attempts were made to measure the rate of polymerisation at temperatures

lower than -19°. However, this was practically impossible, for the following reasons: In order to obtain reasonable rates, the acid concentrations had to be raised considerably; when the acid phial was crushed into the monomer solution, a violent reaction ensued, causing a large part of the monomer to polymerise almost instantaneously. During this time (a few seconds), owing to the relatively slow diffusion of the acid in the solution, a deep yellow colour was noticeable in the environment of the broken phial; once a proper distribution had been attained, the colour was completely discharged and the rate fell correspondingly to a value to be expected in the given situation. This phenomenon was obviously strictly analogous to that of the final sudden kink on the reaction curve when the colour appeared towards the end of the polymerisation. The initial sudden polymerisation could not be ascribed to a simple concentration effect, and was certainly to be associated with the colour formation; thus in a run at -88° (SGP23, see Table 10), the initial sudden polymerisation, lasting 3 or 4 seconds, consumed approximately half of the monomer, whilst it took about three hours for the rest of the styrene to be polymerised in the colourless solution; at the end the colour appeared again. Reactions carried out at -30° and -70° (Table 10) gave similar results. A typical trace for one of these reactions is shown in Fig. 20.

In the "well behaved" reactions water did not seem to produce any change in rates, as shown by a few runs conducted with "wet" solvent (Run SGP6, Table 7).

However, if a mixture of $HClO_4$ and $H_3O^+ClO_4^-$ (the latter is insoluble in CH_2Cl_2) was used as catalyst, the rates obtained indicated that only the anhydrous acid had acted as catalyst (Run SGP7, Table 7).

A second addition of monomer to the polymerised and coloured solution instantaneously discharged the colour and the polymerisation proceeded with rate constant virtually equal to that of the first reaction; the colour reappeared at the end of the second polymerisation (Run SGP11, Table 8).

The molecular weight of the polymers were very low, but as usual in these kind of polymerisations, increased with lowering of the working temperature.

23 runs were carried out.

3.4 Conductivity.

Ten runs in methylene dichloride at room temperature (18-23°) were performed in the high-vacuum conductivity device described in Chapter 1.

Most of them repeated the conditions of equivalent runs previously carried out in the spectroscopic device (Tables 11 and 12).

Readings of K values could be taken approximately every 10 seconds.

No increase in conductivity was noticeable when the reactants were mixed; the conductivity then increased very slowly during a period of time which closely coincided with the induction period of the spectroscopic runs. At the end of this period a sudden rise in conductivity took place, while the solution turned pink for a short while, then yellow.

The rates of increase in conductivity reproduced well the corresponding rates of increase of D_{424} (Fig. 26). A constant value of K was obtained at the end of this second period; if the solutions were left for a fairly long time (hours), it was noticed that the conductivity started decreasing slowly while the solution acquired fluorescence (peaks at 390 mμ and 410 mμ).

Table 7

Reaction data for calorimetrical runs at 19 ± 0.5°

Run No.	$[st]_o$ (M)	$[HClO_4]_o$ (10^4M)	$10^3 k'$ (sec^{-1})	$\bar{M}_n$
SGP3	0.334	4.30	4.53	540
SGP4	"	6.72	7.17	550
SGP6*	"	13.2	14.0	580
SGP8	"	18.0	19.3	690
SGP7**	"	18.0	10.0	590

From Fig. 21 (see opposite):

$$k_p = \frac{k'}{[HClO_4]_o} = 10.7 \text{ l m}^{-1} \text{sec}^{-1}$$

N.B. k' is the slope of the first order plot (see Fig. 18).

* Wet solvent (vessel pumped out only a few minutes)

** The acid phial contained approximately 50% of $HClO_4.H_2O$ (white crystals) and 50% $HClO_4$.

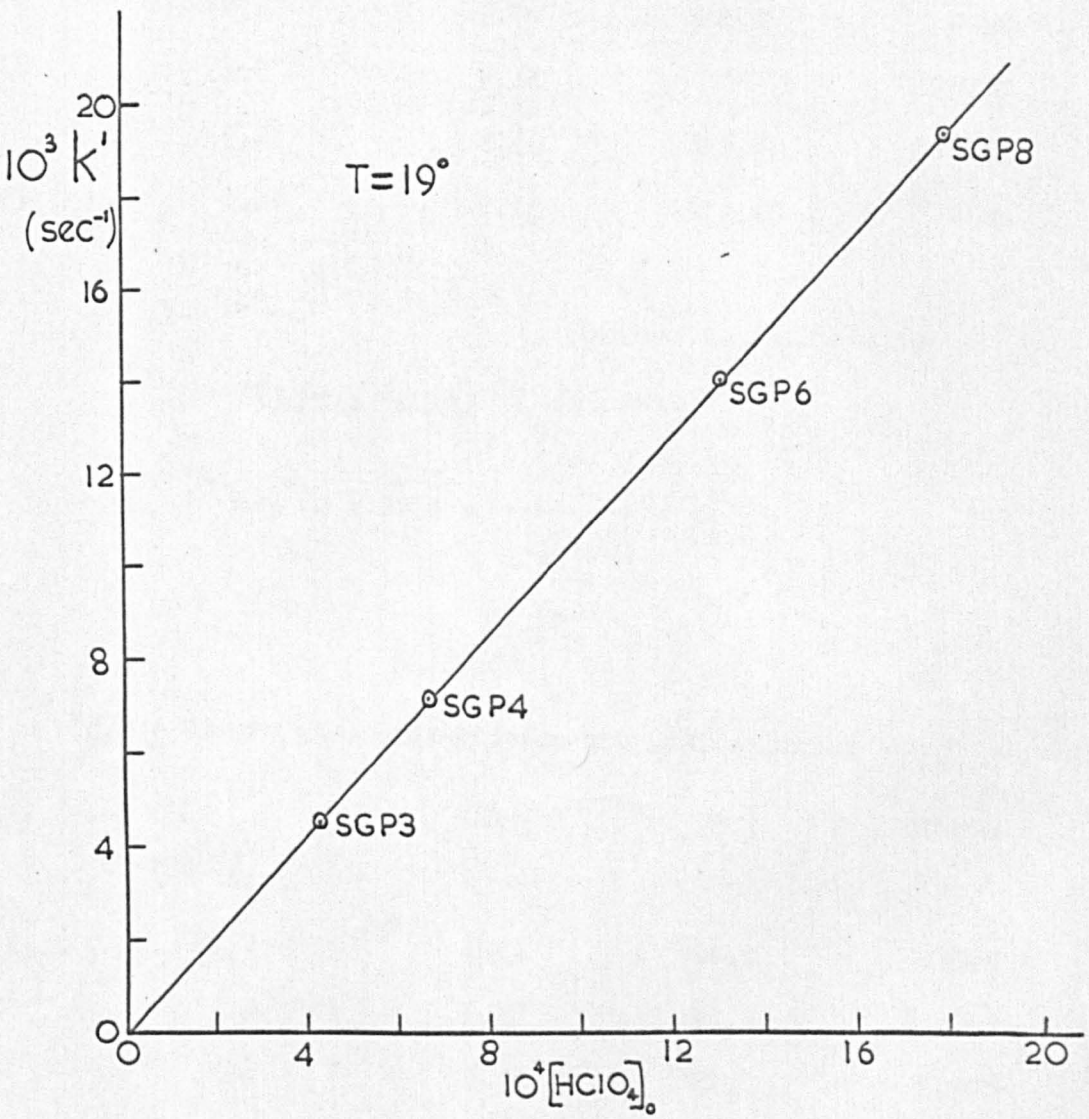

10^3 k'
(sec^{-1})
T=19°
SGP8
SGP6
SGP4
SGP3
20
16
12
8
4
0
0
4
8
12
16
20
$10^4[HClO_4]_o$

Fig. 21

Table 8

Reaction data for calorimetric runs at 0 ± 0.5°

Run No.	$[st]_o$ (M)	$[HClO_4]_o$ (10^4M)	k' ($10^3 sec^{-1}$)	$\overline{M}_n$
SGP9	0.334	17.2	4.60	790
SGP10	"	31.0	8.25	830
SGP11	0.134	55.5	14.7	
SGP11[*]	0.132	54.9	14.2	710

[*]Second addition of styrene

From Fig. 22 (see opposite):

$$k_p = \frac{k'}{[HClO_4]_o} = 2.66 \text{ l m}^{-1} \text{sec}^{-1}$$

Table 9

Reaction data for calorimetric runs at -19 ± 0.5°

Run No.	$[st]_o$ (M)	$[HClO_4]_o$ (10^4M)	k' ($10^3 sec^{-1}$)	$\overline{M}_n$
SGP19	0.226	23.0	1.38	1340
SGP14	0.264	73.0	4.4	1140
SGP17	0.236	91.5	5.5	1000

From Fig. 23 (see opposite):

$$k_p = \frac{k'}{[HClO_4]_o} = 0.603 \text{ l m}^{-1} \text{sec}^{-1}$$

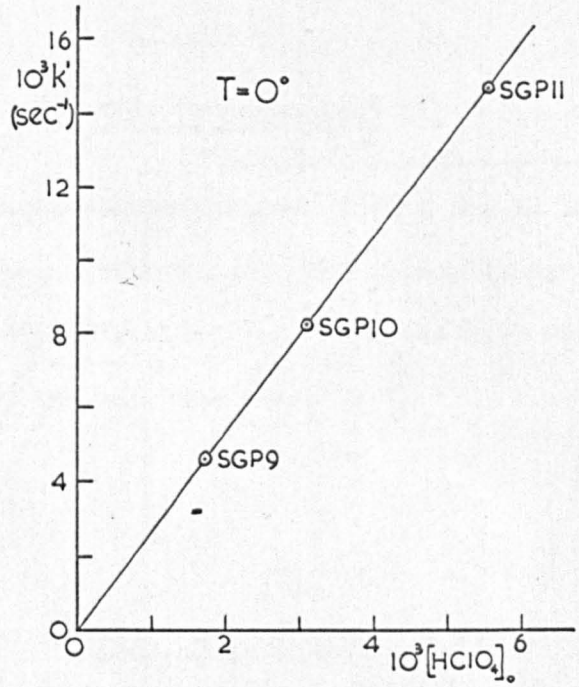

16
$10^3k'$
(sec^{-1})
T=0°
SGP11
12
8
SGP10
SGP9
4
0
0
2
4
6
$10^3[HClO_4]_o$

Fig.22

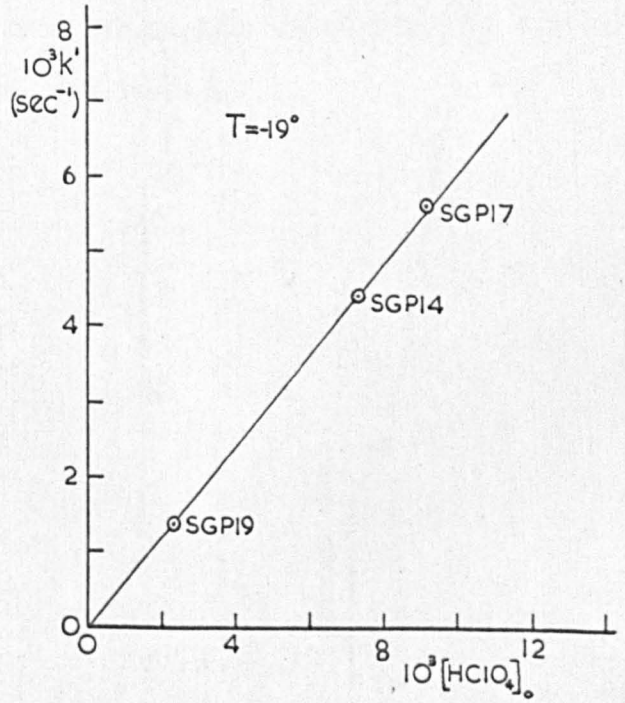

8
$10^3k'$
(sec^{-1})
T=-19°
6
SGP17
SGP14
4
2
SGP19
0
0
4
8
12
$10^3[HClO_4]_o$

Fig.23

Fig.17

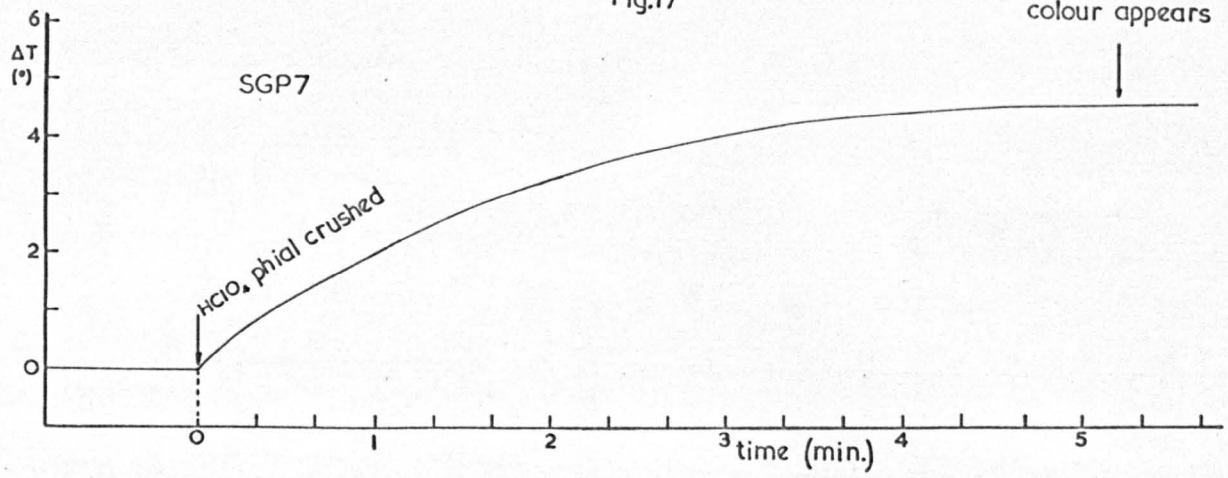

colour appears
ΔT (°)
SGP7
6
4
2
0
HClO4 phial crushed
0
1
2
3
4
5
time (min.)

Fig. 19

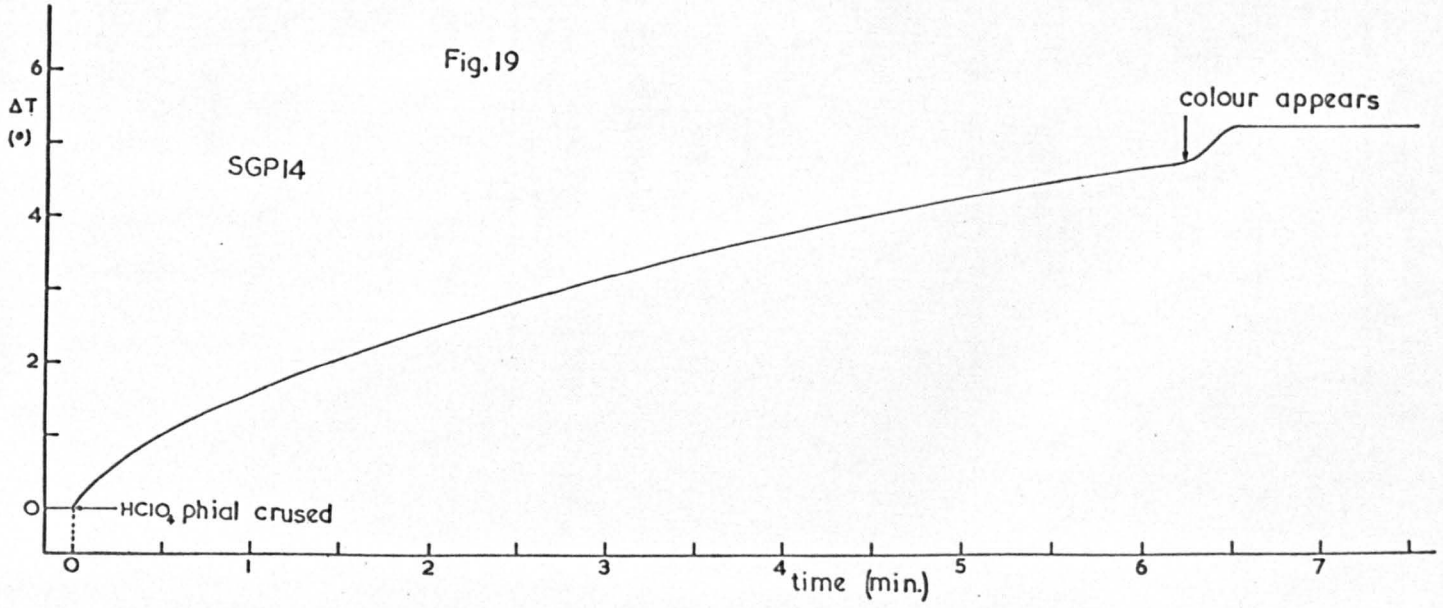

colour appears
ΔT (°)
SGP14
6
4
2
0
HClO4 phial crused
0
1
2
3
4
5
6
7
time (min.)

Fig. 17 (opposite)

A typical polymerisation curve obtained from a run in which the acid concentration was comparatively low. The colour appeared virtually at the end of the polymerisation, i.e. when the heat evolution had ceased. For data on the run, see Table 7.

Fig. 19 (opposite)

A typical run with relatively high acid concentration. The colour appeared at [st] $\lesssim$ 0.027 M, i.e. at [st] $\approx$ 4 $[HClO_4]_o$.
The rest of the styrene was rapidly polymerised in the coloured solution. For data on this run, see Table 9.

Table 10

Reaction data for "anomalous"

calorimetric experiments (see Fig. 20)

Run No.	T (o)	$[st]_o$ (M)	$[HClO_4]_o$ (10^3 M)	$\bar{M}_n$	ΔT^{***} (deg lm^{-1})
SGP15	-19	0.274	14.4	1210	34
SGP18	-19	0.264	18.8	1100	> 80
SGP13	-27	0.163	~6	1020	25
SGP12	-67	0.161	15.0	1300	37
SGP23	-88	0.233	6.93	3040	-
SGP20	-10	0.161	9.0*	609	110

* Total concentration of ClO_4^-; the phial contained the perchlorate salt.

*** The average ΔH for "normal" runs was 23 - 24 deg.l.m^{-1}.

Fig. 18 (opposite)

Typical first order plots obtained from the analysis of "normal" polymerisation curves. Data on the runs are given in Tables 7 and 8.

Fig. 20 (opposite)

A typical run at low temperature with high acid concentration. The colour appeared at the beginning of the reaction, around the crushed phial (a); was then discharged when diffusion occurred (between a and b), and reappeared finally towards the end of the reaction (c). The final kink in the curve is due to the rapid polymerisation of the residual monomer. For data on this run, see Table 10.

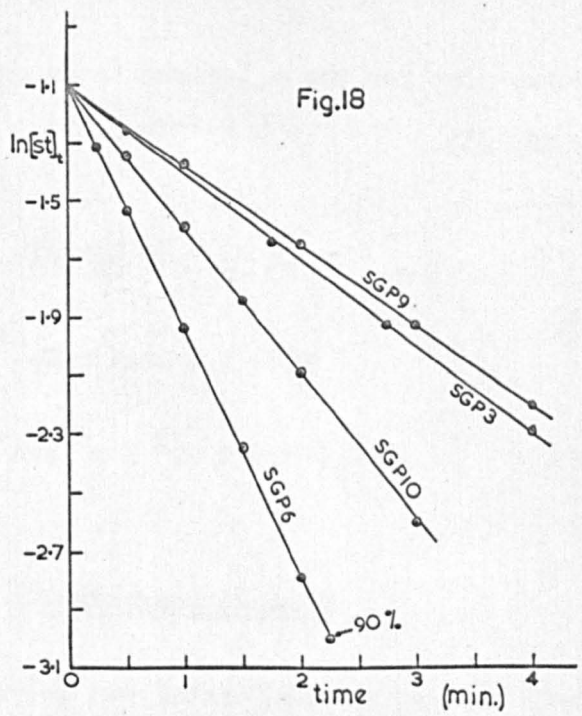


Fig.18
-1·1
ln[st]t
-1·5
-1·9
-2·3
-2·7
-3·1
SGP9
SGP3
SGP10
SGP6
90 %
0
1
2
time
3
(min.)
4

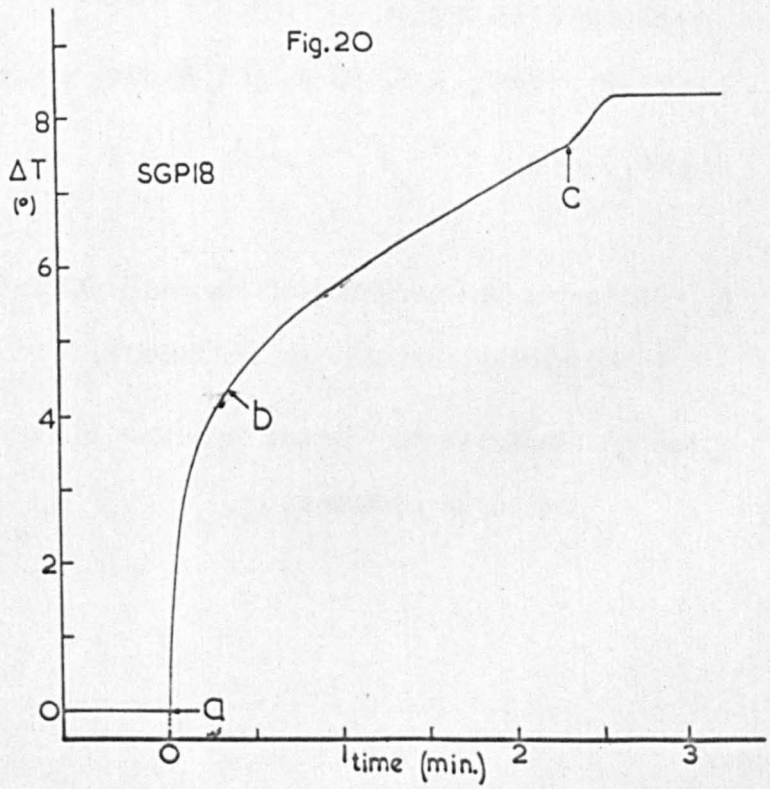


Fig. 20
8
ΔT
(°)
SGP18
6
4
2
0
a
b
C
0
1
time (min.)
2
3

Fig. 24 (opposite)

The Arrhenius plot for the calorimetric experiments (Tables 7, 8, 9 Figs. 21, 22, 23).

$$\ln k_p = \ln A_p - \frac{E_p}{RT}$$

$$E_p = 11.6 \text{ kcal mole}^{-1}$$

$$A_p = 8.9 \times 10^9 \text{ l m}^{-1} \text{sec}^{-1}$$

Fig. 25 (opposite)

A comparison between an $HClO_4$-catalysed polymerisation (SGP11, see Table 8) and one catalysed by an equivalent amount of 1-phenylethyl perchlorate (SGP21).

For SGP21: $[st]_o = 0.158$ M, $[CH_3CHPhBr] = 5.55 \times 10^{-3}$ M

$[AgClO_4] \approx 1 \times 10^{-2}$ M $T = 0^\circ$.

a indicates the crushing of the acid phial (SGP11) and of the 1-phenylethyl bromide phial (SGP21).

b and b' indicate the moment in which the colour appeared in the reaction mixtures.

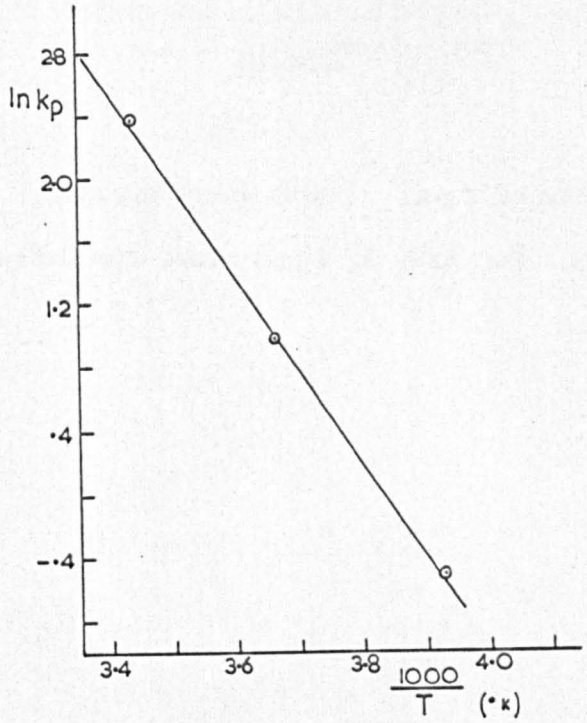

2·8
ln kp
2·0
1·2
·4
-·4
3·4
3·6
3·8
4·0
1000/T (°K)

Fig.24

Fig.25

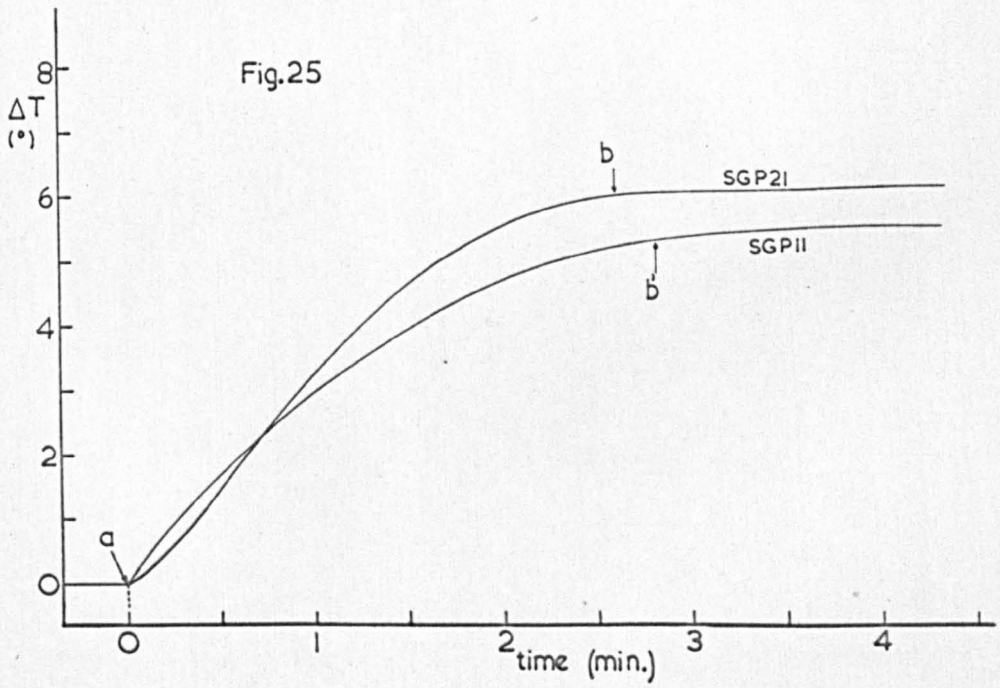
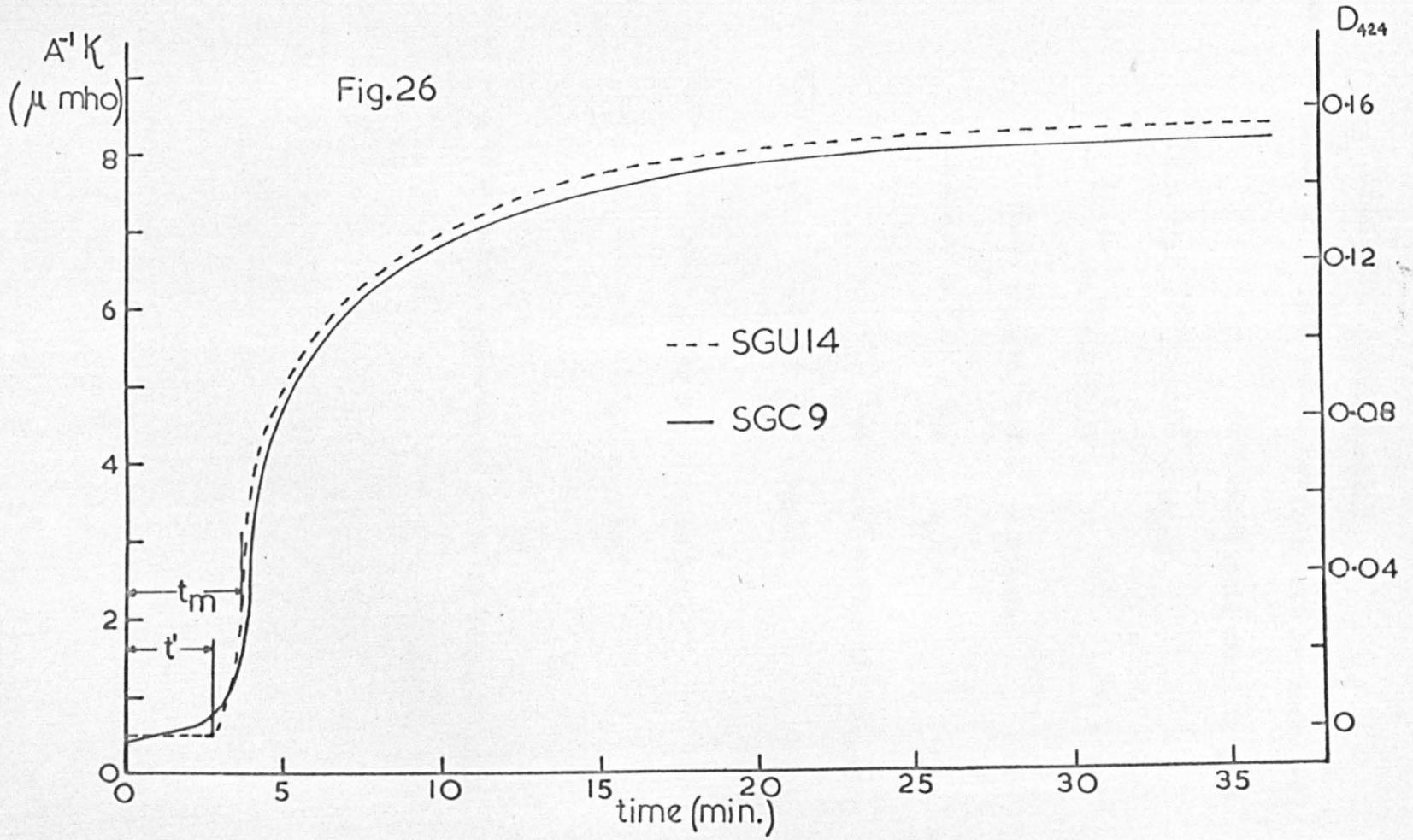

8
ΔT (°)
6
4
2
0
a
b
SGP21
SGP11
b'
0
1
2
3
4
time (min.)

Fig. 26

A typical pair of runs: SGU14 spectroscopic, SGC9 by conductivity. For data on these runs, see Table 11.


A⁻¹K
(μ mho)
Fig.26
D424
0·16
0·12
0·08
0·04
0
8
6
4
2
0
--- SGU14
— SGC9
tm
t'
0
5
10
15
20
25
30
35
time (min.)

Figs. 27 and 28 (opposite)

The amount of free styrene at the end of the induction period.

Fig. 27 (data from Table 11):

$$\text{Slope} = \frac{k_p}{2.3} \times 10^{-3} = 5.15 \times 10^{-3}$$

$$k_p = 11.85 \text{ l m}^{-1}\text{sec}^{-1}$$

$$\text{Intercept} = \log [st]_{t'} = -2.37$$

$$[st]_{t'} = 4.2 \times 10^{-3} \text{ M} \quad n = 4.2$$

Fig. 28 (data from Table 12):

$$\text{Slope} = \frac{-k_p}{2.3} = -5.10 \qquad k_p = 11.73 \text{ l m}^{-1} \text{ sec}^{-1}$$

$$\text{Intercept} = \log [st]_o - \log n = -1.82$$

$$\log n = 0.60 \qquad n = 4.0$$

N.B. Circles refer to spectroscopic runs, triangles to conductimetric runs.

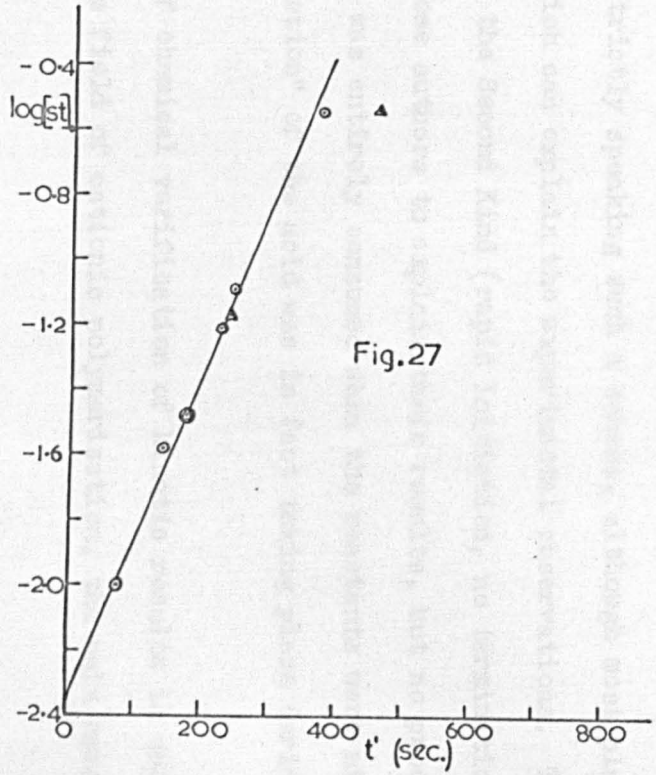

-0·4
log[st]
-0·8
-1·2
-1·6
-2·0
-2·4
0
200
400
600
800
t' (sec.)

Fig. 27

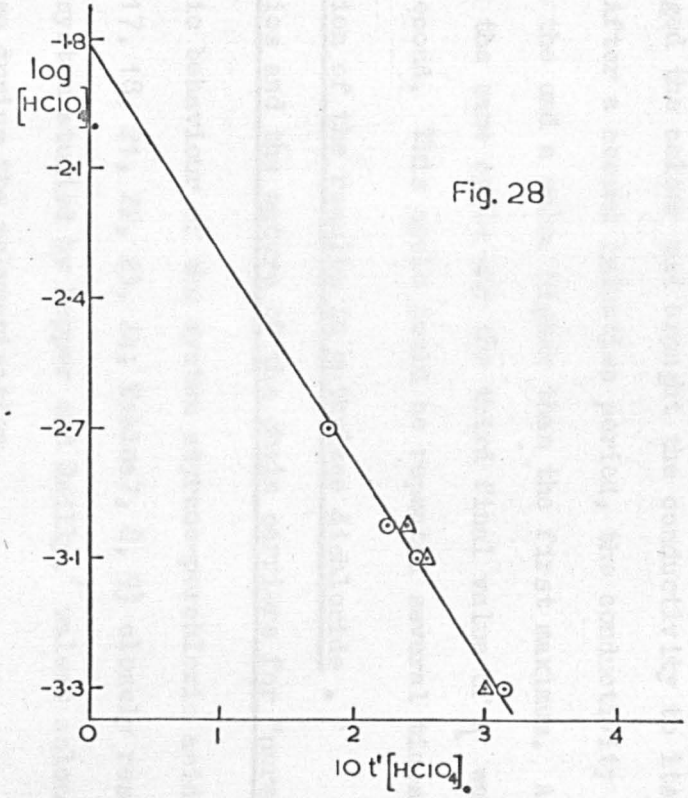

-1·8
log
[HClO4]
-2·1
-2·4
-2·7
-3·1
-3·3
0
1
2
3
4
10 t' [HClO4]

Fig. 28

Addition of a second portion of styrene to the yellow, conducting solution, discharged the colour and brought the conductivity to its initial, very low value. After a second induction period, the conductivity rose again to reach at the end a value higher than the first maximum. A third addition produced the same cycle and the third final value of K_t was yet higher than the second. This cycle could be repeated several times (Fig. 37).

3.5 Interpretation of the results in methylene dichloride .

3.5.1 The kinetics and the nature of the chain carriers for "normal" runs.

The kinetic behaviour of the system styrene-perchloric acid-methylene dichloride (Fig. 17, 18, 21, 22, 23, 24; Tables 7, 8, 9) closely resembles that of the analogous system studied by Pepper and Reilly,[7] unless colour is formed at any stage during the polymerisation.

The reaction scheme put forward by Pepper and Reilly to explain the behaviour of their system has already been shown (see page 6). It must be said here that strictly speaking such a scheme, although most plausible, is not the only one which can explain the experimental observations. The stationary state of the Second Kind (rapid initiation, no termination) was advocated by these authors to explain their results, but no proof was given that the acid was entirely consumed when the reactants were mixed, nor that no "destruction" of the acid was in fact taking place during the polymerisation.

This lack of chemical verification of kinetic results is unfortunately fairly common in the field of cationic polymerisation, the main reasons

for this being the very low concentration of reactants employed (catalyst, as in this case; cocatalyst, more often) which makes it very difficult to detect the reacting species or their reaction products, and the intrinsic complexity of most such systems.

Other reaction schemes can be postulated to explain both Pepper and Reilly's and my results; the following one is the simplest:

$$\text{(initiation)} \quad HClO_4 + M \xrightarrow{k'_i} X^{*} \qquad R_i = k'_i\,[HClO_4]\,[M]$$

$$\text{(propagation)} \quad X^{*} + M \xrightarrow{k'_p} MX^{*} \qquad R_p = k'_p\,[X^{*}]\,[M]$$

$$\text{(termination)} \quad M_nX^{*} + M \xrightarrow{k'_{te}} M_n + Y \qquad R_{te} = k'_{te}\,[X^{*}]\,[M]$$

$$[X^{*}] = \frac{k'_i[HClO_4]}{k'_{te}} \qquad R_p = -\frac{d[M]}{dt} = \frac{k'_p k'_i}{k'_{te}}\,[HClO_4][M]$$

The transfer reactions have been omitted for simplicity, since they do not affect the rate of monomer consumption.

The above interpretation still explains the overall first order of the reaction curves (stationary state of the First Kind), and the external first order with respect to the acid concentration.

I do not want to support this particular scheme, and I cannot offer any reasonable termination reaction in chemical terms. It is essential however to underline that Pepper and Reilly have produced values of k_p which were not proved to be the true values for the propagation rate constant; according to my scheme these values would represent the expression $k'_i k'_p / k'_{te}$.

Two new pieces of evidence have arisen from the present work, which do indeed support Pepper and Reilly's scheme against the second scheme shown above.

a) After one experiment, the polymerised mixture was shaken with aqueous ammonia, and the perchlorate ion concentration in the water layer was determined gravimetrically; 85% of the initial acid could be accounted for by this analysis. Tests for chloride and chlorate ions were negative. Because of the small quantities involved (1 mmole of acid was used) and the absence of the possible degradation products, it was concluded that virtually all the acid (or rather its anion) was still present at the end of the polymerisation. This seemed to rule out the possibility of a termination reaction.

b) A more conclusive piece of evidence came from the polymerisation experiments I conducted with 1-phenylethyl perchlorate as catalyst (see below); according to the evidence I have assembled on the nature of the chain carriers in the present system, which will be discussed later in this Chapter, the polymerisations catalysed by the ester should in fact be "carbon copies" of those catalysed by perchloric acid. The results obtained showed that the kind of time-conversion curve obtained with a given ester concentration closely resembled that of a parallel run with the same acid concentration (Fig. 25). This indicated that all the acid was engaged from the beginning of the polymerisation, in agreement with the postulate of a fast and complete initiation.

On the basis of the whole body of evidence obtained, I could now conclude that the slopes of the plots shown in Fig.s 21, 22 and 23 gave the actual values for the rate constant of the propagation reaction, and that the activation energy obtained from the corresponding Arrhenius plot (Fig. 24) referred to the same reaction.

The values of the k_p's and of E_p agree very well with those obtained by Pepper and Reilly, if the comparison is made between solutions having the same dielectric constant; thus for runs at 0° the value of k_p predicted (Fig. 6, Reilly's thesis) for my conditions ($1/D.C. = 0.117$) is 2.6 $l.mole^{-1} sec.^{-1}$, in excellent agreement with the value of 2.66 found by me (Fig. 22).

The transfer reactions, which are very important in this system, as indicated by the low degrees of polymerisation obtained, were not studied in detail, but both double bonds and indane-type ends were detected in the ultraviolet spectra of the polymers. It seems likely that, as in the system studied by Pepper and Reilly, two types of transfer are occurring during the polymerisation:

a) A unimolecular reaction yielding unsaturated polymer and free perchloric acid.

b) A bimolecular reaction involving a growing chain and a molecule of styrene, which yields a polymer molecule with a cyclic indane-type end.

In both cases the liberated perchloric acid will regenerate rapidly an equivalent amount of chain carriers, by reacting with styrene.

The infrared spectra of the polystyrenes obtained from this system

show, in addition to the peaks typical of "normal" polystyrene, peaks at 6.75 and 7.05 μ given by the indane end-groups.[9] If the polymers had been heated in the presence of air and of the neutralised catalyst, an additional band at 7.95 μ, due to carboxylic groups, formed by oxidation of the terminal double bonds, showed in the spectra.

The agreement between my results and those reported by Pepper and Reilly comes to an end when one starts considering the chemistry of the system rather than its kinetics.

As already mentioned, these two authors formulated a chemical interpretation of their reactions entirely based on carbonium ions (paired to the perchlorate anions); they postulated that the rapid initiation corresponded to a complete consumption of perchloric acid in the protonation of styrene; the 1-phenylethyl ions formed were supposed to be the chain carriers in this system.

Our evidence, substantiated by qualitative and quantitative observations obtained from the use of three independent techniques, shows unequivocally that the "normal" polymerisation (i.e. that which proceeds at relatively low, reproducible speed in absence of colour) must be promoted by active species which are <u>not</u> carbonium ions (free or paired). Figures 17 and 26 clearly illustrate this assertion, and it must be pointed out that they represent typical runs, chosen at random out of a perfectly consistent body of evidence which amounts to some 50 runs.

Moreoever, the substantial agreement obtained from spectroscopic and conductimetric runs, which extends to all the features of the reactions

(See Table 11 and 12 and all the plots derived from them; see also Figure 26), emphasizes the remarkable reproducibility of features shown by this system.

Styryl (polystyryl) ions do appear towards the end of the polymerisation, and this explains why Pepper and Reilly "saw" them and thought that they had a proof for their interpretation, but this formation of ions has virtually nothing to do with the polymerisation itself. I shall comment on this particular phenomenon later on in this Chapter; for the moment I will start by considering the problem of the nature of the chain carriers in the "normal" polymerisation.

The initiation reaction, which involves all the perchloric acid present in the system and some of the styrene, does not yield styryl ions; two other possible routes are envisaged for this reaction, on the basis of general considerations:

a) The interaction of acid with monomer could result in the formation of a π-complex; the only possible way of writing this species consists in placing the acid molecule, or its two ions tightly bound, somewhere near the olefinic double bond. (A proton-double bond complex cannot be formed since in that case we would obtain conducting solutions from the beginning of the polymerisation, owing to the presence of free ClO_4^- ions). This possibility is very difficult to check, but seems also very unlikely. No evidence can be found in the literature for polymerisations catalysed by a π-complex; on the other hand the π-complex of styrene with tetracyanoethylene, which is very easily prepared in methylene dichloride solutions and is

very stable, does not polymerise styrene.[10]

b) Styrene and perchloric acid could react to give the ester 1-phenylethyl perchlorate, which then acts as active species for the polymerisation of the rest of the styrene.

I decided to test the second idea, which seemed to me more reasonable, and also because this seemed more feasible than to test the first one.

Burton and Praill,[11] in a series of publications dealing with acylation and related reactions, have developed a simple route for preparing acyl- and arylperchlorates. Although these were never isolated, the reaction products obtained showed irrefutably that they had been formed in solution as the first step of a series of reactions. The method of preparing aryl perchlorates consisted in making a benzene solution of silver perchlorate react with the given aryl chloride; the reaction product which was thought to exist essentially as ion pairs $Ar^{+}ClO_4^{-}$, interacted with the solvent yielding the corresponding aryl-benzene.

Since my aim was to attempt the preparation of the ester as such, benzene was discarded as possible solvent, and so were other hydrocarbons. Methylene dichloride does not dissolve $AgClO_4$, but it was found that a solution of 1-phenylethyl bromide in this solvent was capable of dissolving a certain amount of the silver salt. It was therefore decided to carry out the reaction under these conditions, rather than to introduce a second solvent, which would have enhanced the polarity of the medium and thus the possibility of ionisation of the ester. (The usual practice in these

instances is to add a little nitromethane to solubilise the $AgClO_4$).[12]

The following procedure was adopted. A phial containing a few millimoles of 1-phenylethyl bromide was placed in a glass tube together with an equivalent amount of $AgClO_4$ and a magnetic breaker; the tube was connected through a fine sintered-glass filter to the usual "tipping" device (see Chapter 1). After sealing the tube, the whole device was attached to the solvent dispensing and vacuum system; during the pumping out, the silver perchlorate was warmed to about 90° in order to remove any moisture it might contain. After four hours of hard vacuum, the pumping line was closed and about 15 ml of methylene dichloride was run into the device, which was then sealed off. The bromide phial was crushed and good mixing applied to the device: the reaction started immediately, and the solution turned yellow-orange. The colour of the solution became deeper and deeper, whilst silver bromide accumulated at the bottom of the tube. After about one hour of good shaking the solution, which was by now very dark brown-orange, was filtered through the sintered glass into the flask of the tipping device and frozen. The tipping device was sealed from the rest of the apparatus, the liquid was allowed to thaw and was then tipped into the twelve phials, which were in turn sealed off by the described technique (Chapter 1).

In order to check upon the extent to which the reaction had proceeded two of the phials were crushed in an aqueous solution containing an excess of NaOH; the colour was completely and instantaneously discharged on mixing. Back titration of the excess base indicated that the ester

formation had proceeded to 90-95% conversion.

The organic layer from the titration checks was isolated, and the solvent evaporated; the residue appeared to be low molecular weight polystyrene. An ultraviolet spectrum of this polymer showed the presence of two sharp peaks at 390 and 410 mμ respectively.

One of the phials was diluted in a second "tipping" operation and one of the phials thus obtained was placed in the usual spectroscopic device. After the normal series of operations, a visible spectrum of the light brown solution was taken: together with the two peaks just mentioned, the spectrum exhibited a third broad peak with $\lambda_{max} \simeq 470$ mμ. Through a break seal mounted on the device, a large excess of styrene was added to the brown solution: the colour was immediately discharged, while the solution warmed up considerably; after about two minutes the colour started reappearing: the spectrum showed a peak at 424 mμ which in a few minutes was shifted to a broad peak centred at about 475 mμ. The final D_{475} was higher than that obtained from the original solution. The polymer obtained for this run had $\overline{DP} = 6$. The situation can be summarised as follows:

a) The reaction of silver perchlorate with 1-phenylethyl bromide proceeds to near completion yielding probably 1-phenylethyl ions at first (yellow-orange colour observed at the beginning of the reaction); some of these ions form subsequently, with their anions, perchloric acid and styrene. The styrene produced is polymerised. The ultimate result of this series of reactions closely resembles the state of affairs at the end of a styrene polymerisation run

catalysed by perchloric acid: a twin peak in the near visible portion of the spectrum and a broad peak at about 470 mμ.

b) Addition of styrene to the ionic solution obtained from the reaction, suppresses the ions while the added monomer polymerises, as when a second addition of styrene is made to a polymerised, coloured solution after a "normal" polymerisation run. The colour re-emerges at the end of the polymerisation, and its final intensity is, as in the corresponding case of a spectroscopic run, higher than it was before the styrene addition.

The conclusion was that the ester prepared by a one-to-one reaction of $AgClO_4$ with 1-phenylethyl bromide is mainly present as ions (or ion pairs), and that only an excess of styrene seems capable of stabilising it. No proof could be obtained from these experiments for an ester-catalysed polymerisation, simply because the situation which I came to be dealing with was not different from that at the end of a run carried out with styrene and $HClO_4$.

The idea of the ester being stabilised by an excess of styrene seemed however, worth investigating further. I decided therefore to prepare the ester by the described reaction, but in the presence of an excess of styrene; in other words, to carry out a polymerisation run in which the alledged initiator would be prepared <u>in situ</u>.

Into the reaction calorimeter two phials were placed, one (at the top of the holder) containing styrene, the other containing a known amount of 1-phenylethyl bromide in CH_2Cl_2. A slight excess of $AgClO_4$ (with

respect to the bromide) was placed in the reaction vessel. After four hours of hard pumping, methylene dichloride was run into the calorimeter. The apparatus was cooled to 0°.

The concentrations were chosen so as to reproduce the conditions of a run performed with perchloric acid as catalyst (Run SGP 11), except for $[st]_o$ which was 0.16 M instead of 0.134 M.

The styrene phial was crushed and good stirring applied to the solution for about 15 minutes in order to bring as much silver perchlorate as possible into solution. After having equilibrated the solution temperature, the bromide phial was crushed under good stirring: the solution immediately became turbid (whitish precipitate of silver bromide) and polymerisation started.

No colour was generated during virtually the whole of the polymerisation, but the usual golden yellow colour, following a transitory pink coloration, appeared towards its end and became then deeper and deeper.

The reaction curve obtained from this run is shown in Fig. 25, together with that obtained from the corresponding run SGP 11. The initial sigmoid shape of the "ester" curve can easily be accounted for, considering that during that time the reaction between the silver salt and the bromide was still proceeding and that therefore the concentration of chain carriers was increasing.

The time-conversion scale is virtually the same for the two curves.

A second experiment was carried out under these conditions, with a lower "ester" concentration and gave similar results. Again the agreement of the reaction trace with the equivalent one obtained from an acid catalysed polymerisation, was very satisfactory.

The $\overline{DP}$'s of the polymers obtained from these runs were the same as those of polymers from acid catalysed runs.

N.B. Anhydrous silver perchlorate was found to interact with undiluted styrene to give approximately 10% polymerisation in a few hours. This effect is however negligible compared with the type of time-conversion curves which the present system gives.

The extent to which a molecule of ester needs to be "solvated" by free styrene so that it will not ionise, was obtained in the first instance from the runs with final kink due to ionic polymerisation; by measuring the conversion at which the colour appeared, I was able to estimate that approximately four molecules of styrene monomer per molecule of catalyst were still present in the polymerising solution when the carbonium ions started to appear (Fig. 19). However, a better method of evaluating the free monomer present at the end of the induction period was worked out. Since the disappearance of styrene follows the rate equation (1)

$$-d[st]/dt = k_p[st][HClO_4]_o \qquad (1)$$

it follows that

$$\log [st]_o - \log [st]_t = k_p [HClO_4]_o t/2.3 \qquad (2)$$

If one assumes that the number of free styrene molecules at t = t' is a multiple n of the number of chain carriers which is equal to the number of acid molecules introduced,

$$[st]_{t'} = n\,[HClO_4]_o \qquad (3)$$

equation (2) takes the form:

$$\log [st]_o - \log n - \log [HClO_4]_o = k_p\,[HClO_4]_o t'/2.3 \qquad (4)$$

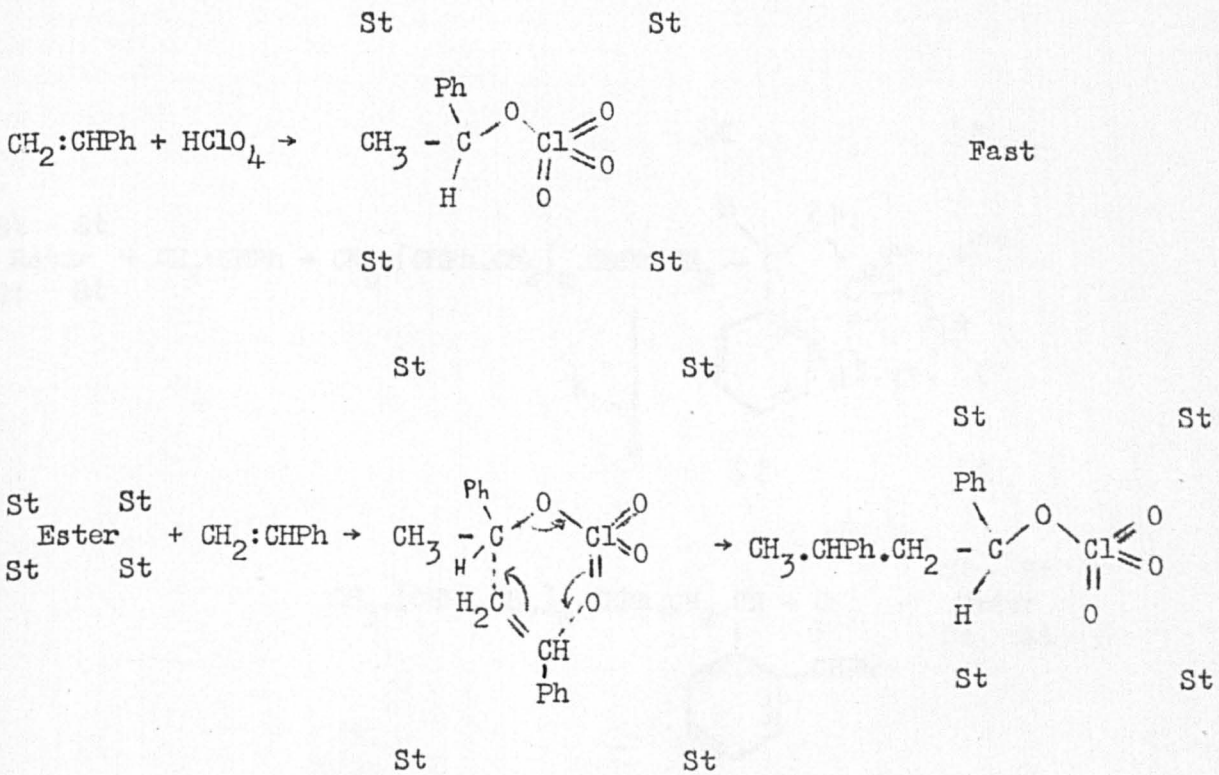
where t' is the time at which ions start to be formed.

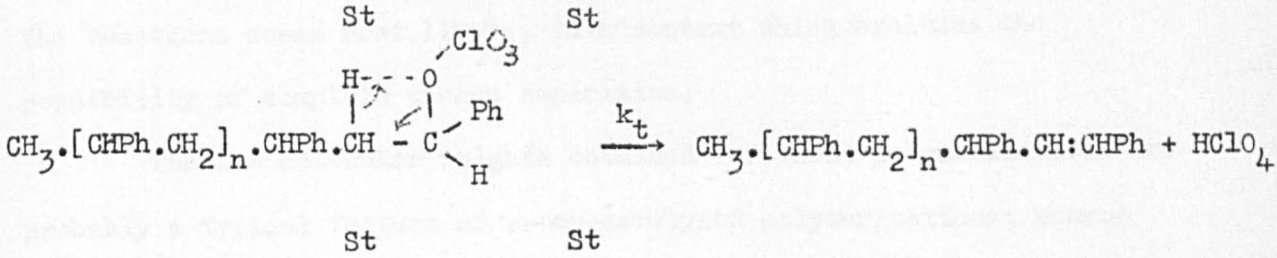
The values of t' obtained in series of spectroscopic and conductimetric experiments conducted at constant $[st]_o$ and at constant $[HClO_4]_o$ respectively (Table 11 and 12) can now be plotted according to equation (4). For runs at constant $[st]_o$ a plot of $\log [HClO_4]_o$ against $[HClO_4]_o t'$ should give a straight line with slope $-k_p/2.3$ and intercept $\log [st]_o - \log n$. For runs at constant $[HClO_4]_o$, a plot of $\log [st]_o$ against t' should again give a straight line with slope $k_p/2.3\,[HClO_4]_o$ and intercept $\log [st]_{t'} = \log [HClO_4]_o + \log n$.

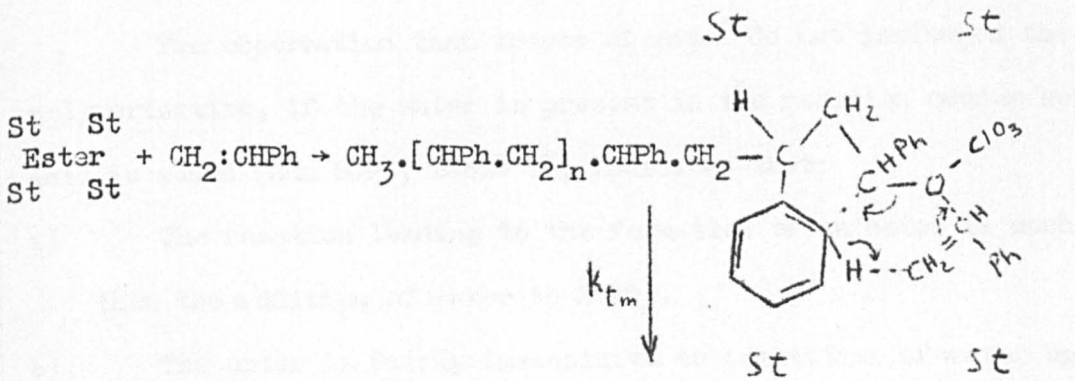
Figures 27 and 28 show that straight lines are in fact obtained; from the slopes, values of k_p are obtained (11.8 and 11.7 respectively); these values are in excellent agreement with the value of 11.7 obtained from the calorimetric results (this value is read off Fig. 24, for the working temperature of 22°). This confirms the validity of the procedure; the values of n obtained from the intercepts are both very close to 4.0.

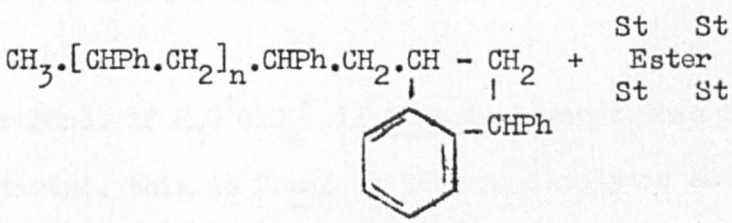
The conclusion is therefore that four molecules of styrene monomer are necessary to stabilise one ester molecule.

The question arises now: How does an ester molecule propagate a chain? From the evidence I have collected, and on the basis of more general considerations concerning possible non-ionic chain-carriers and the corresponding transitions states (among others, Fontana[13] has recently given some attention to this general problem), the following scheme of reactions can be written:









The actual location of the four monomer molecules which contribute to the stabilisation of the ester is still obscure, and they have been therefore placed arbitrarily around it, just to make clear that they are needed for the reactions to be <u>non-ionic</u>.

The formation of an even-membered cyclic transition state during the reactions seems most likely, in a context which excludes the possibility of complete charge separation.

The low molecular weights obtained for these polymerisations are probably a typical feature of ester-catalysed polymerisations; Monroe and Gilliland[14] formulated an ester-type mechanism for the high pressure oligomerisation of propylene catalysed by dilute phosphoric acid. Also, it seems likely that the oligomerisation of isobutene in methylene dichloride, catalysed by anhydrous perchloric acid,[15] proceeds via an ester intermediate.

The observation that traces of water do not influence the rate of polymerisation, if the water is present in the reaction medium before the acid is added (Run SGP6, Table 7), indicates that:

a) The reaction leading to the formation of an ester is much faster than the addition of water to $HClO_4$.

b) The ester is fairly insensitive to quantities of water up to about 10 times its concentration, i.e. hydrolysis under these conditions is negligible.

On the other hand, if $H_3O^+ClO_4^+$ is <u>already</u> present when the polymerisation is started, this is found to have no catalytic activity, most probably because it is insoluble in methylene dichloride (Run SGP7, Table 7).

A more thorough discussion of the implications of the present findings for the whole chemistry of cationic polymerisations will be given at the end of this Chapter.

3.5.2 The polymerisation catalysed by carbonium ions.

Attention has already been drawn to the anomalous, very high rates of polymerisation obtained when colour (carbonium ions) appears in a polymerising solution. This phenomenon is typified in Figs. 19 and 20.

There does not seem to be any doubt that the fast polymerisation of styrene either in the proximity of the crushed perchloric acid phial, or towards the end of a "normal" run, when there is not sufficient free monomer to stabilise the ester, is the result of the action of very powerful chain carriers, namely the 1-phenylethyl and polystyryl ions.

Up to 80% of the initial monomer was polymerised in some instances within a few seconds from mixing the reactants, just because the acid phial, which contained a relatively large amount of $HClO_4$, necessary to give a conveniently measurable rate of polymerisation if only the ester had been formed, had not been crushed completely, but only punched through. And it is remarkable that the yellow colour formed around the broken phial was not very deep, certainly not as deep as that obtained at the end of that same polymerisation.

Owing to the impossibility of evaluating the actual carbonium ion concentration during these fast reactions and to the fact that the pen trace was virtually perpendicular to the time axis, it is difficult to assess even a rough value for the reaction rate constant for true cationic polymerisation; it can only safely be said that this is at least 100 times greater than the value of k_p for the ester catalysed polymerisation.

The reaction curves obtained for these ionic polymerisations showed that the overall temperature increase was always too high when compared with equivalent "ester" runs (Table 10). This anomalous behaviour has not yet found a reasonable explanation. One possible cause for these (rather large) differences in ΔT might be the fact that the different chain carriers produce polymers with different molecular weight distributions and since the heat of oligomerisation of styrene (dimerisation, trimerisation, etc.) is higher than that of polymerisation (it decreases asymptotically from a maximum for the heat of dimerisation to a virtually constant value for terms higher that decamer), this would produce different overall temperature rises.

No marked difference could be noticed in the average values of $\overline{DP}$, for polymers obtained from runs involving the two different chain carriers. This is not conclusive evidence against the above interpretation, because the determining factor is here the molecular weight distribution; accurate molecular weight measurements must therefore be carried out on the fractionated polymers, before any definite conclusion can be drawn.

A second cause for these discrepancies could come from the fact that polymers with different structure are formed in the two kinds of polymerisation. Accurate I.R. and ultraviolet spectra should reveal any substantial difference in structure between the two polymers; with the techniques employed during this work, such differences could not be detected.

Additional evidence for carbonium ion polymerisation was

provided by a run in which I used a phial of the perchlorate salt (see above) as catalyst. In this run I crushed the catalyst phial first; the styrene phial was then crushed into the deep brown solution. A fast polymerisation ensued, which consumed all the monomer within a few seconds, while the solution remained intensely coloured. If the polymerisation had been catalysed by the corresponding ester concentration (see Table 10, Run SGP2C) at that temperature, it would have required several minutes to go to completion. Under these conditions the styrene diffusing into the solution met a high population of carbonium ions and was therefore polymerised cationically. Polymerisation was so fast that the monomer was consumed before it could depress the carbonium ion concentration and formester molecules.

In the light of the present findings on the true cationic polymerisation of styrene, the observations made by Pepper and Reilly[7] that above a certain acid concentration the kinetics of polymerisation departed from the simple first-order pattern to become more complicated, can now be explained. Addition of large quantities of perchloric acid to styrene probably produced a certain amount of carbonium ions and anomaloies similar to those described in this section altered considerably the kinetic behaviour of the system.

3.5.3 The formation of polystyryl ions.

3.5.3.1 The behaviour of the "dry" systems.

At the end of the induction period t', during which most of the monomer is polymerised, a short transition phase, characterised by the formation and destruction of species absorbing around 510 mμ, preceeds the appearance of the golden-yellow colour, (424 mμ) typical of the polystyryl ions.

Virtually no study has been made of the 510 mμ peak because of its short life, and therefore I cannot offer a firm interpretation of it. However, it seems likely that it is due to an intermediate between the stable chain carriers (in presence of excess of free styrene) and the polystyryl ions which begin to appear soon after the end of the induction period.

The effect of the initial acid concentration (at constant $[st]_o$, Table 12) and of the initial styrene concentration (at constant $[HClO_4]_o$, Table 11) on the rate of production of polystyryl ions, was studied by scanning at fixed wavelength (424 mμ) against time, at room temperature. The reaction curves obtained from these runs (Fig. 26) were analysed as follows:

a) The induction period t' was measured and related to the initial concentration of the reactants. The resulting plots (Figs. 27 and 28) have already been interpreted in the preceeding section.

b) The maximum rate, R_m^+, obtained by drawing a tangent to the curve at the inflection point which occurred after a short acceleration

was measured together with the time t_m at which it occurred.

c) A full kinetic analysis of each curve was carried out both for the first order (plot of log (1 - p) against time, p being the per cent. conv.) and for the second order with equal initial concentration, of reactants (plot of 1/(1 - p) against time). Figure 29 illustrates the results obtained for a typical curve. The slopes S_1 and S_2 of the straight portions of these plots were recorded.

d) The final, maximum values of D_{424} and of K_L were obtained.

N.B. For runs with relatively high $[st]_o$ (i.e. $[st]_o > 0.2$ M), the formation of allylic ions (see next Section) and their typical peak around 450 mμ started very soon after the end of the induction period, namely while D_{424} was still increasing. This phenomenon produced anomalous D_{424}-time curves since the tail of the 450 mμ peak (which was as intense as that at 424 mμ) interfered strongly at 424 mμ and D_{424} increased monotonically instead of following the typical pattern shown in Fig. 26. For these runs therefore, only the values of t', t_m and R_m^+ could be obtained (see Runs SGU10, 11, 12 and 13, Tables 11 and 12). It was not possible to correct for the absorption at 450 mμ because of lack of information about that peak.

The parameters thus obtained, tabulated in Tables 11 and 12, were used on the basis of the following considerations: The reactions which give rise to the carbonium ions probably involve the ester, free perchloric acid and unsaturated polymer chains (it has been shown that

perchloric acid does not interact with substituted indanes; see Section 2.1.). Since there is no termination, the acid introduced at the beginning of the reaction is still present at this stage in the form of ester or free; on the other hand the styrene has all been polymerised by the time the carbonium ions start appearing. One cannot therefore relate the reaction features of the polystyryl ion formation to the initial styrene concentration; instead, the concentration of polymeric double bonds at the end of the polymerisation, or some value proportional to it, should be derived, since this would be the relevant variable to be related to the reaction parameters.

In order to obtain the concentration of double bonds I have assumed that Pepper and Reilly's[7] findings on the transfer reaction are qualitatively valid for my system. These authors found that the spontaneous transfer, which is of first order with respect to growing chains, yielded unsaturated polymer molecules, whilst transfer with monomer gave dead polymer molecules with indane end-groups.

If these findings can be applied to my system, which, after all, differs only in the solvent from that studied by Pepper and Reilly, the rate of double bond formation can be written:

$$\frac{d\,[DB]}{dt} = k_t\,[E] \qquad (1)$$

where [DB] indicates the double bond concentration and [E] the ester concentration <u>during the polymerisation</u>. For the period of the polymerisation t', during which $[E] = [HClO_4]_o$ = constant, the equation

can be integrated to the form:

$$[DB]_t = k_t [HClO_4]_o \, t \qquad (2)$$

Thus the double bond concentration in the polymerising solution is just directly proportional to the time.

At $t = t'$, only two species relevant to the ionogenic reaction will be present, namely the polymer ester ($[E] = [HClO_4]_o$) and polymer molecules containing a double bond ($[DB]_{t'} = k_t [HClO_4]_o \, t'$).

At the end of the polymerisation, i.e. at $t \geq t'$, the ester molecules will still continue to produce chains with double bonds according to the same reaction, the only difference being the fact that the acid liberated will not be able to find any more styrene with which to reform the ester. To a first approximation equation (2) can be extended to the accelerating part of the ion-formation curves and one can therefore write:

$$[DB]_{tm} = k_t [HClO_4]_o \, t_m \qquad (3)$$

The free acid formed after t' is the third species relevant to the reaction under study: its concentration will increase progressively from 0 at $t = t'$ to a maximum value at the end of the reaction (see scheme below).

The rate of ion formation R^+ can be related to the concentrations which are known in the present instance by the general relation:

$$R^+ \equiv \frac{d[P_n^+]}{dt} = k_1 [DB]^x [HClO_4]^y \qquad (4)$$

and from eqn. (2):

$$R^+ = k_t^x \, k_1 \, [HClO_4]_o^{x+y} \, t^x \qquad (5)$$

At time t_m, the rate reaches a maximum value:

$$R_m^+ = k_t^x \, k_1 \, [HClO_4]_o^{x+y} \, t_m^x \qquad (6)$$

and

$$\log R_m^+ = \log k_t^x \, k_1 + (x+y) \log [HClO_4]_o + \log t_m \qquad (7)$$

Also, from eqn. (4),

$$\log R_m^+ = \log k_1 + x \log [DB]_{tm} + y \log [HClO_4]_o \qquad (8)$$

Equations (7) and (8) can be used to relate the experimentally found values of R_m^+ to the concentration of acid, at constant $[DB]_{tm}$, and to the maximum concentration of double bonds, at constant $[HClO_4]_o$.

A plot of $\log R_m^+$ against $\log t_m$, for runs at constant $[HClO_4]_o$ (eqn. 7) should give a straight line with slope equal to x, i.e. the order in double bond concentration for the initial part of the ion formation reaction. By using the data given in Table 11, I obtained a plot with a slope of unity, so I replotted directly R_m^+ against t_m and obtained a straight line passing through the origin (Fig. 30). Thus $x = 1$.

From Table 12 it can be seen that for runs at constant $[st]_o$,

$[DB]_{tm}$, which is given by the product $k_t[HClO_4]_o\ t_m$ is roughly constant, since the product $[HClO_4]_o\ t_m$ does not change sensibly for the series of runs conducted. A plot of log R_m^+ against log $[HClO_4]_o$ should be a straight line and give as slope the order in acid (ester) at constant [DB] (eqn. 8) for the initial part of the reaction. This is in fact true as shown in Fig. 31; the order in acid is about 2 for both plots, referring to the two series of runs conducted. Thus y = 2. The experimental rate equation for the initial part of the ionogenic reaction is therefore:

$$R_m^+ \doteq \left(\frac{d[P_n^+]}{dt}\right)_m = k_1\ [HClO_4]_o^2\ [DB]_{tm} \qquad (9)$$

It can be seen from eqn. (7) that unless k_t is known, the value of k_1 cannot be computed from the intercept of the plots given in Figs. 30 and 31. Unfortunately, I have not done experiments aimed at the computation of k_t and $[DB]_{tm}$.

After the very first part of the reaction, i.e. at $t > t_m$, the situation becomes more complicated because the double bonds present in the systems start being removed from it by a cyclisation reaction catalysed by the free perchloric acid present at that stage.

The kinetic details of this reaction, which yields indane end-groups are not known, and this prevents a full treatment of the present situation.

The formal kinetic analysis of the curves (Fig. 29) was carried out by neglecting the short period of acceleration, i.e. by drawing the curves artificially back to zero $[P_n^+]$ from the point of inflection.

Since the acceleration part was always a very small portion of

the whole curve, this approximation seemed justified for a first approach to the problem.

The first part of the curves gave a straight line when $1/(1-p)$ was plotted against t (Fig. 29). This can be expressed as:

$$\frac{dp}{(1-p)^2} = k_2 [P_n^+] \, dt \qquad (10)$$

where p is the conversion expressed as the ratio $\frac{[P_n^+]}{[P_n^+]_m}$, and k_2 is a composite constant including probably the equilibrium constants for the relevant reactions, given below.

Equation (10) is only valid in the part of the curve for t' to t_b, the time at which the change in order takes place. After t_b, the plot of log (1-p) against time is linear, showing that a new relationship now holds, viz.

$$\frac{dp}{1-p} = k_3 \, dt \qquad (11)$$

this being valid from t_b to $t = \infty$.

The correlation of the slopes S_1 and S_2 of the groups of plots, with the relevant concentrations (viz. $[HClO_4]_o$ and $[DB]_{tm}$) gave the following results.

a) For the first part of the reaction (second order with equal starting concentration, equation (10)), S_2 was directly proportional to $[HClO_4]_o$ at fixed $[DB]_{tm}$ (Fig. 32) and inversely proportional to

$[DB]_{tm}$ at fixed $[HClO_4]_o$ (Fig. 33).

b) For the second part of the reaction (first order, eqn. (11)), S_1 was directly proportional to $[HClO_4]_o$ at fixed $[DB]_{tm}$ (Fig. 34) and independent of $[DB]_{tm}$ at fixed $[HClO_4]_o$ (Fig. 35).

A scheme of reactions and equilibria has been derived for the system under study; I have taken into consideration all the experimental evidence given above and the two important facts reported below:

I At the end of the ionogenic reaction, i.e. when conductivity and D_{424} have attained a maximum, constant value, there are still double bonds present in the system, which is revealed by the ultraviolet spectra taken at that time.

II The final conductivity increases considerably as the temperature is reduced from 23° to 0° (Runs SGC 9, Table 11, and SGC11, Table 12).

These observations indicate clearly that the reactions studied go to equilibria and not to completion.

The scheme is given below.

Once all the monomer has been consumed, reaction (12),

$$E \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} HA + DB \qquad (12)$$

$$K' \equiv \frac{k_t}{k_{-t}} = \frac{[HA][DB]}{[E]} \qquad (13)$$

continues to proceed but, as mentioned above, the free acid [HA] formed

does not find any more styrene with which to regenerate the ester. Thus, the acid interacts with the ester itself to give carbonium ions, which are stable only if solvated by a molecule of acid:

$$HA + E \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} P_n^+HA + A^- \qquad (14)$$

$$R^+ \equiv \frac{d[P_n^+HA]}{dt} = k_3 [HA] [E] \qquad (15)$$

$$K'' \equiv \frac{k_3}{k_{-3}} = \frac{[P_n^+HA]^2}{[HA] [E]} \qquad (16)$$

while the polymerisation proceeds ($t \leqslant t'$) the material balance, referred to the acid present takes the simple form

$$[HClO_4]_o = [E]$$

At $t > t'$ the material balance becomes:

$$[HClO_4]_o = [HA] + [E] + [P_n^+HA]$$

Both reactions (12) and (14) reach equilibrium, the respective constants being given by the equations (13) and (16).

From equations (13) and (15) one obtains

$$R^+ \equiv \frac{d[P_n^+HA]}{dt} = k_3[HA]^2[DB]/K' \qquad (17)$$

If at time t_m equilibrium (12) lies far to the left, i.e. if $[HA]_{tm} \approx [HClO_4]_o$, equation (17) will satisfy the experimental findings summarised in equation (9), for the maximum rate of ion formation; k_1 will be the ratio k_2/K'.

The very first accelerating part of the ion-formation ($t' < t < t_m$) is explained by the fact that during that time reaction (12) is proceeding towards equilibrium and an increasing number of free acid molecules is being produced, thus giving a sigmoid curve for the formation of ions (eqn. (14)).

The maximum rate R_m^+ occurs when reaction (12) has reached equilibrium and the consumption of double bonds by cyclisation is still small.

After thispoint ($t > t_m$) the reaction curve reflects a complicated set of reactions involving the formation of ions (eqn. (14)) and the concurrent, and competitive (with respect to the acid, probably) consumption of double bonds by the cyclisation reaction.

The first portion of the curve seems to be overall second order (equal initial concentrations); however, this means very little at present, since one does not know the relative concentrations of the reactants, namely [DB], [E] and [HA]. The relationships obtained between S_2 and $[HClO_4]_o$ and $[DB]_{tm}$ respectively are therefore difficult to interpret and have a merely qualitative value. The inverse proportionality found for the double bonds (Fig. 33) seems to indicate that the cyclisation reaction involves an important part of the acid, and therefore the more

double bonds are present, the less free acid will be available for the ionogenic reaction (14).

The second part of the reaction (first order, see Fig. 29), seems to be clearer; once most of the double bonds have been removed by cyclisation, equilibrium (12) will be shifted far to the right so that most of the acid will again be "free; the consequence of this will be that reaction (14) takes place between a large excess of free acid, and a small amount of ester and will therefore be virtually first order, since the acid consumption is nelgigible. This assumption requires that the slope S_1 of the first order plot must be independent of [DB] and directly proportional to the total acid concentration $[HClO_4]_o$, for under these conditions $[HA] \approx [HClO_4]_o$ because [E] and $[P_n^+HA]$ are both very much smaller than $[HClO_4]_o$. These are precisely the experimental findings (Figs. 34 and 35). From Fig. 34, which shows that $S_1 = k_3[HClO_4]_o/2.303$, a value of $k_3 = 2.45$ l m^{-1} $sec.^{-1}$ is obtained at room temperature.

From the eqns. (13) and (14) always assuming that $[HA] \approx [HClO_4]_o \gg E$ at the end of the ionogenic reaction, one gets:

$$\frac{K'}{K''} = \frac{[HA]^2[DB]}{[P_n^+HA]^2} \qquad (19)$$

Unfortunately, this relationship cannot be fully tested with my experimental results because I do not know the value of [DB] at the end of the reactions, since for most runs the polymer concentration at the end of the ionogenic reaction was too high for a spectrum in the ultraviolet region to be obtainable.

A plot of the final ionic concentration against the initial acid concentration, for runs performed at constant $[st]_o$ is shown in Fig. 36. It is a straight line for the lower $[HClO_4]_o$ but becomes markedly curved at higher $[HClO_4]_o$. If equation (11) is valid, Fig. 36 indicates that the double bond concentration at the end of the reaction is virtually the same for the runs which give the straight portion of the plot, whilst it decreases when the acid concentration is increased above a certain value (curved portion). This behaviour is probably to be ascribed to the fact that at higher $[HClO_4]_o$ the cyclisation reaction becomes more and more important and the double bond concentration is reduced accordingly.

N.B. The concentrations of polystyryl ions $[P_n^+]$ were computed assuming that ε_{424} is the same as ε_{427} for the 1-phenylethyl carbonium ion (Table 6).

The following considerations can be given in support of the present interpretation of the experimental results:

a) I have already mentioned the observations which indicate that both reactions (12) and (14) go to an equilibrium.

b) The final concentration of polystyryl ions is always much lower than the corresponding $[HClO_4]_o$; this means either that equilibrium (14) lies far to the left, or, more probably, that equilibrium (12) lies either far to the right and therefore [E] is very small (and consequently $[P_n^+]$ is very small) or far to the left thus giving a very small [HA] (and consequently a very small $[P_n^+]$).

The kinetics of ion formation strongly support the conclusion that the reactant present in the smallest concentration is the ester; if, on the contrary, one assumes that the free acid concentration is the lowest, the kinetic relationships one derives are in strong disagreement with the experimental observations.

c) Reaction (10) has been written on the basis of Pepper and Reilly's evidence,[7] for a system closely similar to mine, which in other respects, such as the kinetics of propagation, the influence of water, etc. is in excellent qualitative and quantitative agreement with my results. Reaction (14) which shows that free acid is needed for an ester to ionise because the carbonium ion is stable only when solvated by a molecule of acid, is not the first of this kind. Evans and his co-workers[16] have postulated similar reactions to explain their results on the dimerisation of 1,1-diphenylethylene catalysed by trichloroacetic acid; the spectroscopic evidence offered by these authors seems to indicate that the reaction involves carbonium ions, and the kinetics of the dimerisation showed that the order in acid was always greater than one. The reaction of carbonium ion formation was written as involving three molecules of acid, two of which were thought necessary to solvate the ion.

d) If the polymer solution is left under vacuum for several hours after the end of the ionogenic reaction, the polymer recovered contains virtually no double bonds (ultraviolet spectroscopy); this indicates that the cyclisation reaction goes to completion. During that time,

the polystyryl ion concentration decreases and D_{424} goes virtually to 0 at the end (see Section 3.2.1). Since the double bonds are steadily removed by the cyclisation reaction, Equilibrium (12) is in fact never attained; moreover, as the double bonds are consumed, less and less ester is present in solution. Towards the end of the reaction $[P_n^+]$ should start decreasing, and as the cyclisation reaction is completed, no more secondary polystyryl ions should be present in the system because Equilibrium (14) should be shifted completely to the left. This has been found to happen, but over a period of several hours, probably because the cyclisation reaction reaches completion slowly, over the same length of time. The fact that we observed a constant value of $[P_n^+]_m$ over a period of several minutes is probably due to the interference of the allylic ion peak which grows during that time while D_{424} starts decreasing; as pointed out earlier in this section, once the allylic peak starts appearing, the exact computation of the actual value of D_{424} becomes impossible.

The conductivity remains constant for a few minutes at the end of the ionogenic reaction (Fig. 26); this is probably due to the irreversible formation of ionic impurities (see Section 3.5.5) which counter balances the decrease due to the slow disappearance of polystyryl ions. After a few hours however, the conductivity does decrease, indicating that $[P_n^+]$ is strongly reduced as a consequence of the cyclisation reaction. The whole situation can be schematically depicted as follows:

$$A^- + P_n^+HA \underset{HA}{\rightleftharpoons} E \rightleftharpoons DB + HA \rightarrow Cy + HA$$

$$\downarrow$$

Allylic ions (see Section 3.5.4)

where Cy is the indane end-group.

It must be pointed out that, although the proposed scheme of reactions and equilibria has not been fully checked by the experimental evidence, mainly because the cyclisation reaction proceeding concurrently with the formation of carbonium ions has not been studied, this is the only scheme among the several simple ones tried, which is not in conflict with any piece of evidence obtained and which satisfied many of the observations.

3.5.3.2 The influence of added water.

The influence of added water upon the ionogenic reaction was studied only spectroscopically; the results obtained are given in Table 13. When the water added gave $[H_2O] \approx 5[HClO_4]_o$, no carbonium ions at all were formed at the end of the polymerisation (run SGU17); this shows once again the strong destructive effect of water on these ions. When $[H_2O] \approx \frac{1}{3}[HClO_4]_o$, both the rate of ion formation and the final ionic concentration were considerably lower than those obtained for a "dry" run (compare SGU9 and SGU20, Table 13). At the end of the polymerisation, when free acid is formed, the water present in solution, which had had no effect on the actual polymerisation (see Section 3.5.2), reacts with an equivalent amount

of $HClO_4$ to form $H_3O^+ClO_4^-$; this compound is inactive as ionising agent. If therefore $[H_2O] > [HClO_4]_o$ no ions will be formed, all the free acid regenerated being converted to its monohydrate; if $[H_2O] < [HClO_4]_o$, the rate of polystyryl ion production and $[P_n^+]_m$, which both depend on $[HClO_4]_o$, will be reduced because the active acid concentration will only be $[HClO_4]_a = [HClO_4]_o - [H_2O]$.

3.5.3.3 The limiting equivalent conductance.

In the range of carbonium ion concentrations studied (10^{-5}-10^{-4} M) the relative concentration of ion pairs (non-conducting species) is negligibly small; this is born out by a comparison of the spectroscopically computed ionic concentrations (sum of free ions and ion pairs) at the end of the reactions and the final values of electrical conductivity for the parallel runs (Tables 11 and 12). The plot of K against the ionic concentration $[P_n^+]_m$ is in fact a straight line passing through the origin, which shows that I was dealing with free ions only; if there had been important quantities of ion-pairs this plot would have been markedly curved, since the higher the total ionic concentration, the lower the equivalent conductance. From the slope of this plot a value for Λ_o at room temperature (23 - 24°) was computed as:

$$\Lambda_o = \frac{1000\,K}{[P_n^+]_m} = 17.3 \text{ mho cm}^2 \text{ mole}^{-1}$$

Λ_o is the sum of the limiting equivalent conductances of the

polystyryl ion (Λ_o^+) and of the perchlorate anion (Λ_o^-).

Mason[12] found for triphenylmethyl perchlorate in 1,2-dichloroethane at 21.5° a Λ_o of 66.5 mho cm^2 $mole^{-1}$. The large differnece between these two values, apart from the different solvent involved and the slight difference in temperature is due to the following two factors:

a) The polystyryl ion has a much smaller mobility than the triphenylmethyl carbonium ion, and will contribute very little to the total conductance.

b) The viscosity of my polystyryl solutions is much higher than that of pure methylene dichloride. This is certainly the main cause for the large difference in Λ_o, and makes comparisons of my value with published ones rather pointless, since I cannot evaluate the necessary correction factors.

The interest of the present value for Λ_o lies in the fact that it represents a useful guide for further study on systems of this kind, involving viscous polymer solutions; it will help in the computing of approximate values of carbonium ion concentrations from conductivity measurements.

Table 11

Spectroscopic (SGU) and conductimetric (SGC) runs at fixed initial acid concentration; solvent CH_2Cl_2, room temperature.

Run No.	$[st]_o$ (10^2M)	$[HClO_4]_o$ (10^3M)	t' (sec)	t_m (sec)	R_m^+ (10^5 m l^{-1} min^{-1})	R_m^+ (μMho min^{-1})	$[P_n^+]_m$ (10^5M)	$(\Lambda^{-1})_m$ (μMho)	S_2 (10^3 sec^{-1})	S_1 (10^4 sec^{-1})
SGU25	1.0	1.00	75	105	0.98		1.35		16.0	11.3
SGU18	2.6	"	140	180	1.68		3.44		14.0	10.5
SGU14	3.3	"	175	200	2.02		3.96		13.2	11.5
SGC9	3.3	"	175	200		3.9		8.14 (10.2*)	10.2	10.5
SGU16	6.2	"	225	295	2.72		10.18		7.3	11.6
SGC8	6.7	"	240	300		5.2		16.5	7.3	13.3
SGU15	8.1	"	245	330	3.19		12.38		5.1	10.2
SGU13	28.6	"	375	450	3.44		-		-	-
SGC7	29.0	"	460	530		8.1		38.3	2.4	5.0

*Value at 0°

Table 12

Spectroscopic (SGU) and conductimetric (SGC) runs at fixed initial styrene concentration; solvent CH_2Cl_2, room temperature.

Run No.	$[st]_o$ (10^2M)	$[HClO_4]_o$ (10^4M)	t' (sec)	t_m (sec)	R_m^+ (10^5m l^{-1} min^{-1})	R_m^+ (μMho min^{-1})	$[P_n^+]_m$ (10^5M)	$(\kappa A^{-1})_m$ (μMho)	S_2 (10^3 sec^{-1})	S_1 (10^4 sec^{-1})
SGU21	6.1	5.0	630	840	0.54		4.66		2.9	5.0
SGC10	6.1	5.0	600	700		1.06		7.90	2.8	5.3
SGU23	6.2	8.0	310	380	1.45		7.51		4.6	9.4
SGC11	6.1	8.0	320	400		3.00		11.13(14.0*)	6.1	9.7
SGU16	6.2	10.0	225	300	2.72		10.18		7.3	11.6
SGC8	6.7	10.0	240	300		5.2		16.5	7.3	13.3
SGU22	6.1	20.0	85	120	9.07		11.86		14.3	20.7
SGU12	33.0	4.3	1260	1350	0.31		-		-	-
SGU10	35.0	8.7	700	800	2.10		-		-	-
SGU11	34.0	12.0	450	540	3.37		-		-	-

*Value at 0°.

Fig. 29 (opposite)

A typical kinetic analysis of a reaction curve for polystyryl ion formation.

N.B. The second order plot implies equal initial concentration for the two reactants.

Run SG09 (see Table 11)

The change from second to first order takes place at $\approx$ 300 seconds, at p $\approx$ 70% .

Fig. 30 (opposite)

The dependence of maximum rate of ionic formation, R_m^+ , upon the double bond concentration at fixed $[HClO_4]_o$.

(see Table 11)

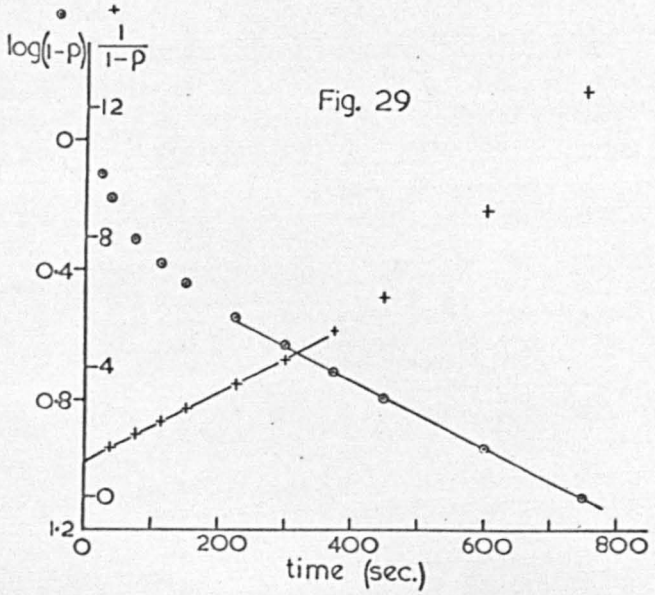

log(1-p)
1/(1-p)
1·2
0·8
0·4
0
12
8
4
0
0
200
400
600
800
time (sec.)

Fig. 29

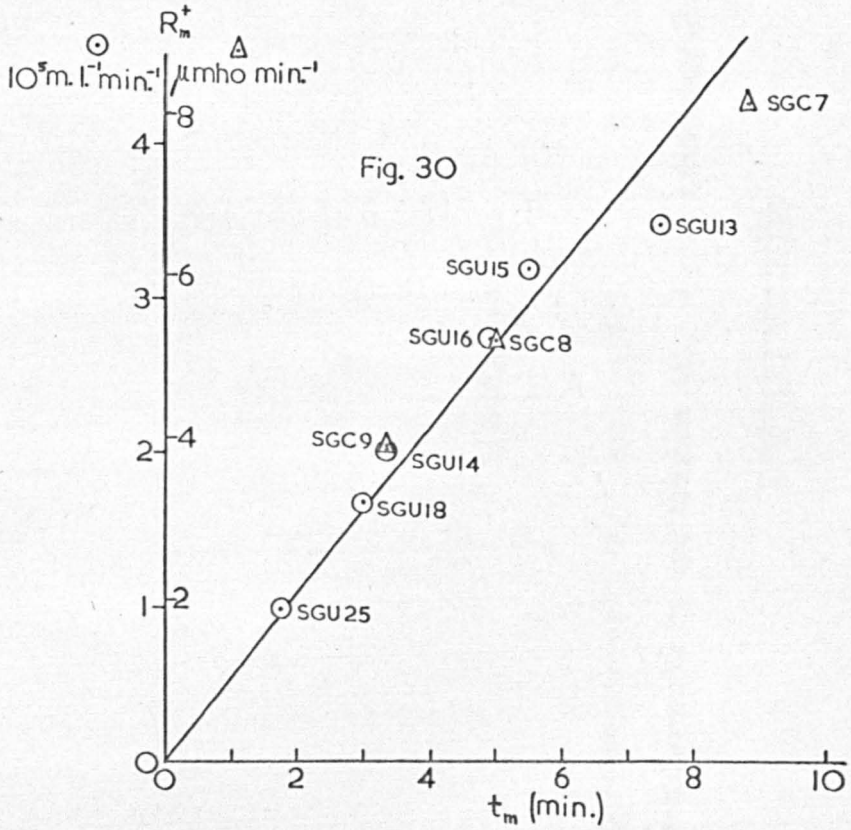

R+m
⊙ 10⁵m. l.⁻¹min.⁻¹
Δ μmho min.⁻¹
8
6
4
2
0
3
2
1
0
2
4
6
8
10
tm (min.)
SGC7
SGU13
SGU15
SGU16
SGC8
SGC9
SGU14
SGU18
SGU25

Fig. 30

Fig. 31 (opposite)

The dependence of the maximum rate of ion formation upon the initial acid concentration, at fixed $[DB]_{t_m}$.

(see Table 12)

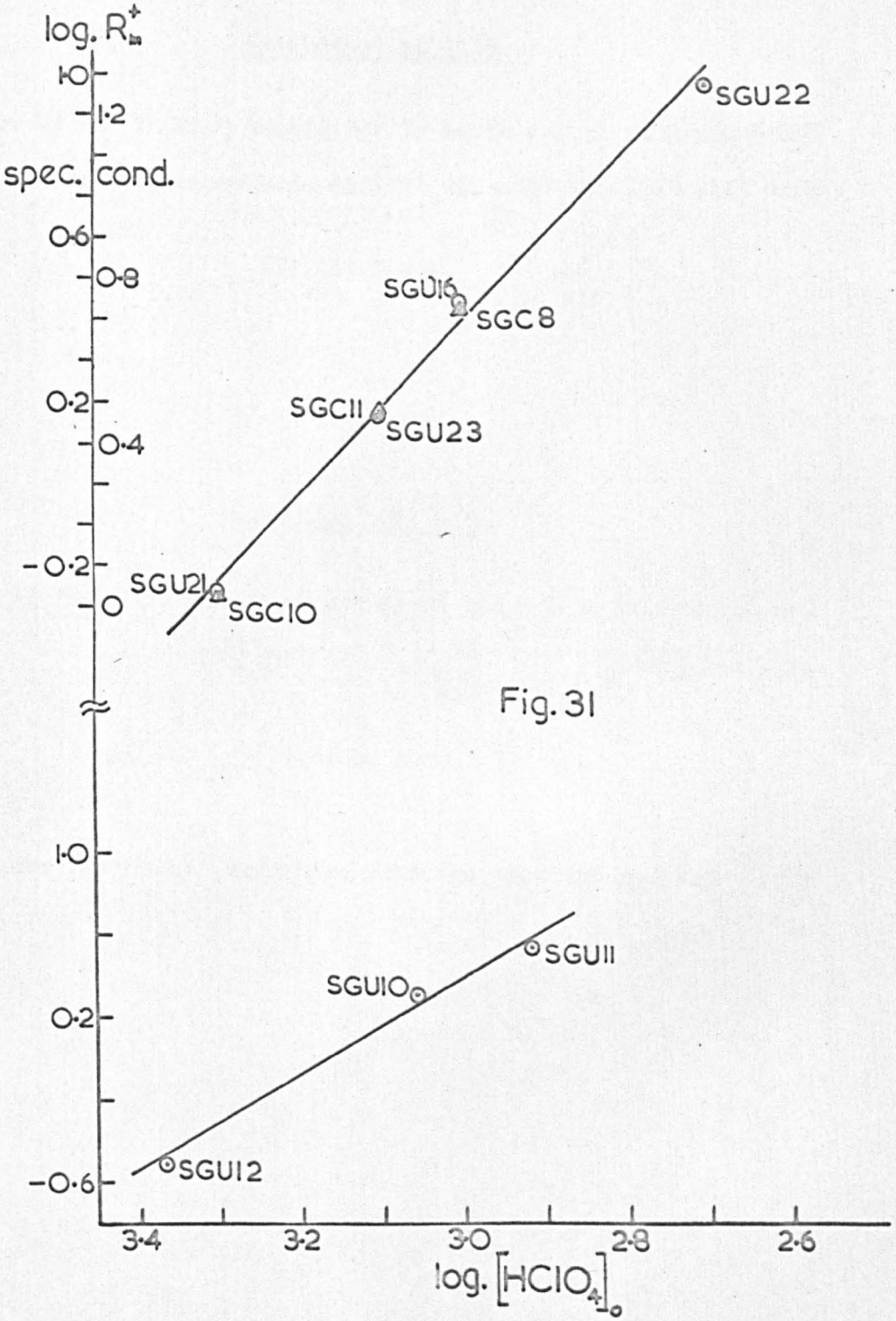

log. R_m^+
1·0
1·2
spec. cond.
0·6
0·8
0·2
0·4
−0·2
0
1·0
0·2
−0·6
SGU22
SGU16
SGC8
SGC11
SGU23
SGU21
SGC10
SGU11
SGU10
SGU12
3·4
3·2
3·0
2·8
2·6
log. $[HClO_4]_o$

Fig. 31

Fig. 32 (opposite)

The dependence of the slope of the linear part of the second order plot (see Fig. 29) upon the initial acid concentration.

(see Table 12)

Fig. 33 (opposite)

The dependence of S_2 upon the maximum concentration of double bond, at fixed $[HClO_4]_o$

(see Table 11)

N.B. Circles indicate spectroscopic runs, triangles conductivity runs.

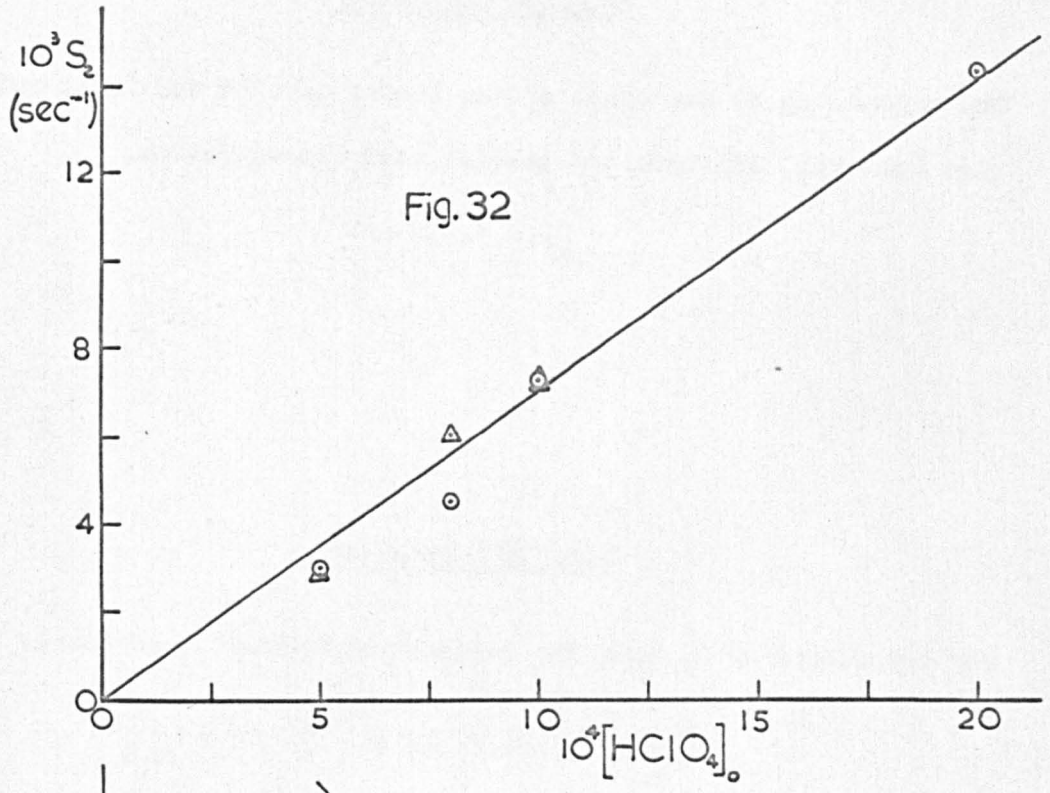

$10^3 S_2$ (sec^{-1})
12
8
4
0
0
5
10
15
20
$10^4[HClO_4]_o$

Fig. 32

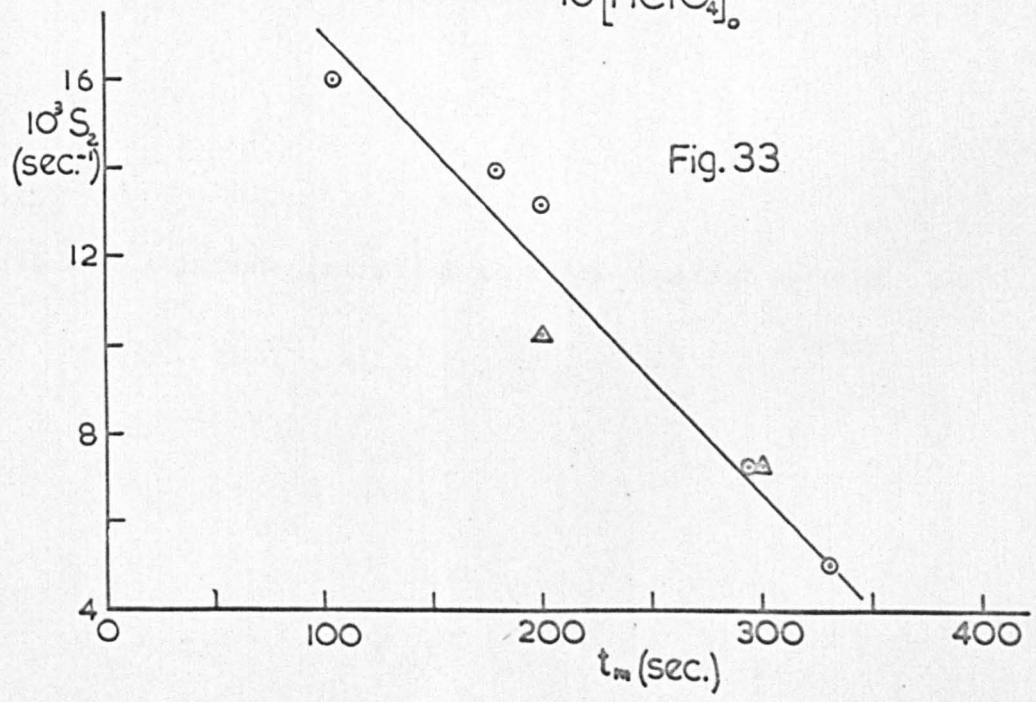

$10^3 S_2$ (sec^{-1})
16
12
8
4
0
100
200
300
400
t_m (sec.)

Fig. 33

Fig. 34 (opposite)

The dependence of the slope of the linear part of the first order plot (see Fig. 29) upon the initial acid concentration.

(see Table 12)

Fig. 35 (opposite)

The dependence of S_1 upon the maximum concentration of double bonds.

(see Table 11)

N.B. Circles indicate spectroscopic runs, triangles conductivity runs.

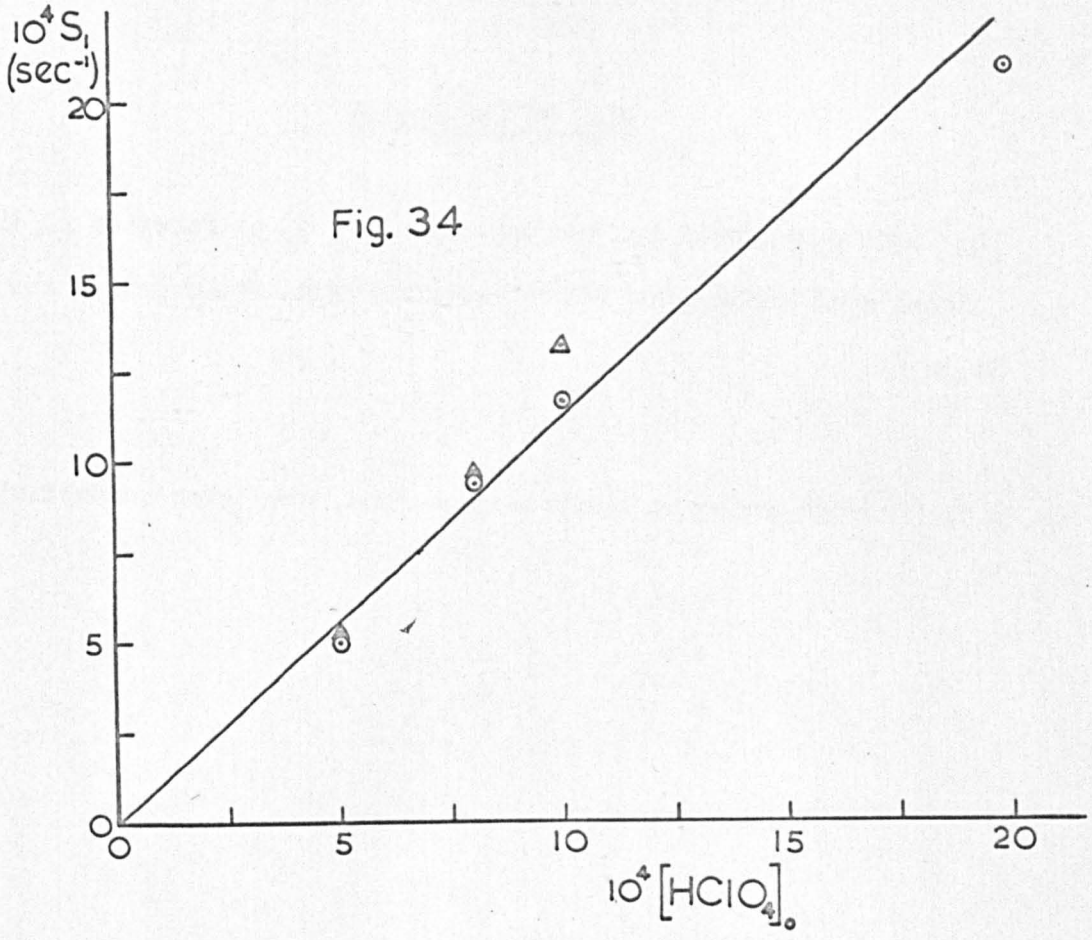

$10^4 S_i$ (sec^{-1})
20
15
10
5
0
0
5
10
15
20
$10^4 [HClO_4]_o$

Fig. 34

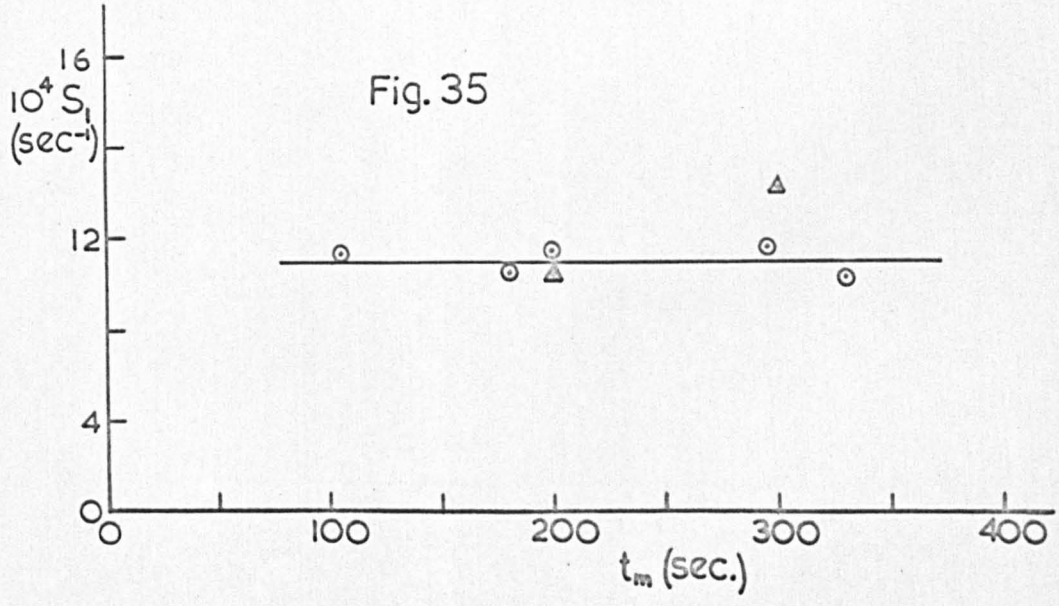

$10^4 S_i$ (sec^{-1})
16
12
4
0
0
100
200
300
400
t_m (sec.)

Fig. 35

Fig. 36 (Opposite)

The final polystyryl ion concentration $[P_n^+]_m$ as function of the initial acid concentration for experiments at fixed $[st]_o$; see Table 12.

N.B. Circles indicate spectroscopic runs, triangles conductivity runs.

FIG. 36

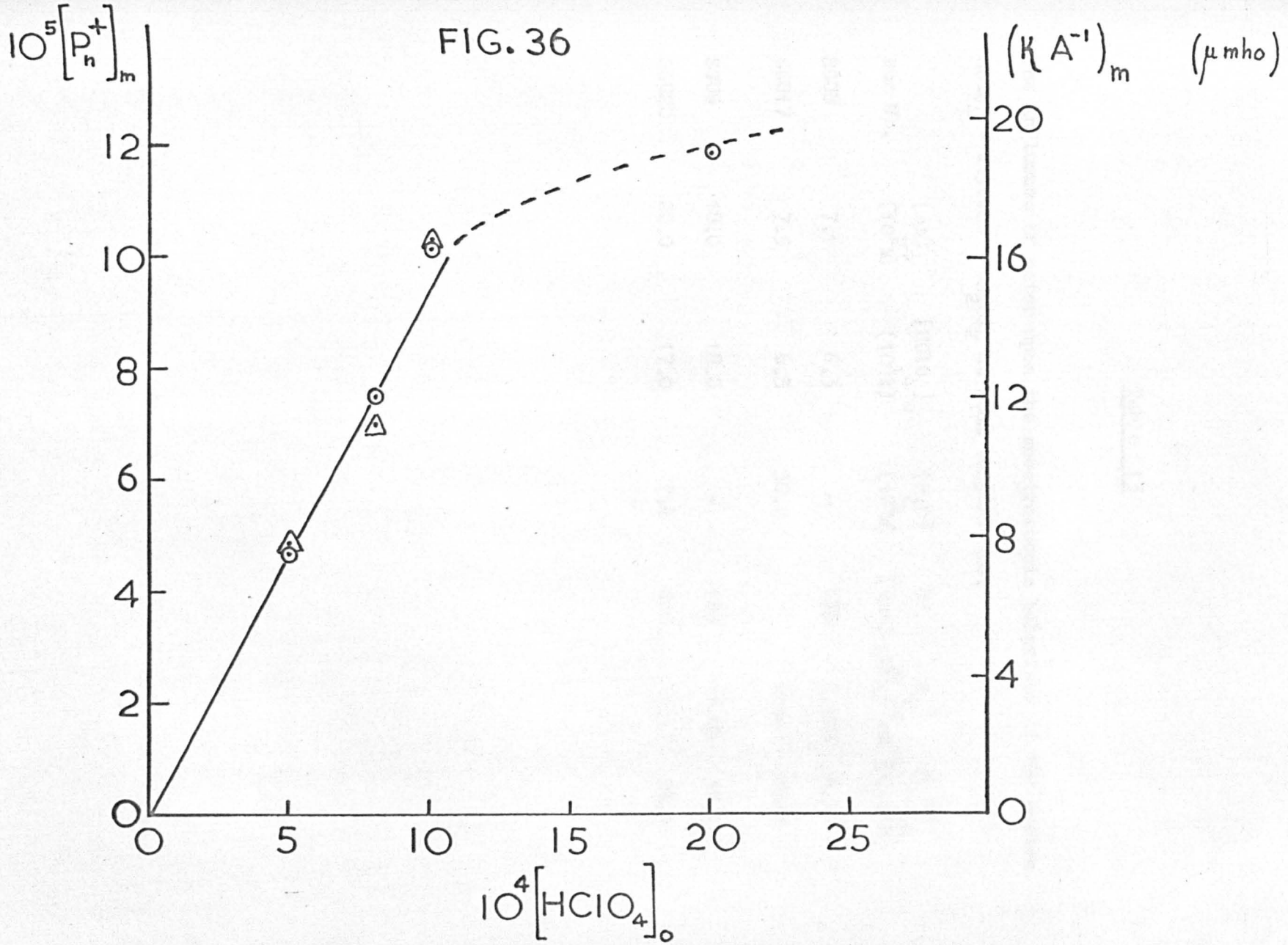

$10^5[P_n^+]_m$
$(K A^{-1})_m$ (μmho)
0
2
4
6
8
10
12
0
4
8
12
16
20
0
5
10
15
20
25
$10^4[HClO_4]_o$

Table 13

The influence of water upon the spectroscopic behaviour of the system $HClO_4$ - styrene - CH_2Cl_2 at room temperature.

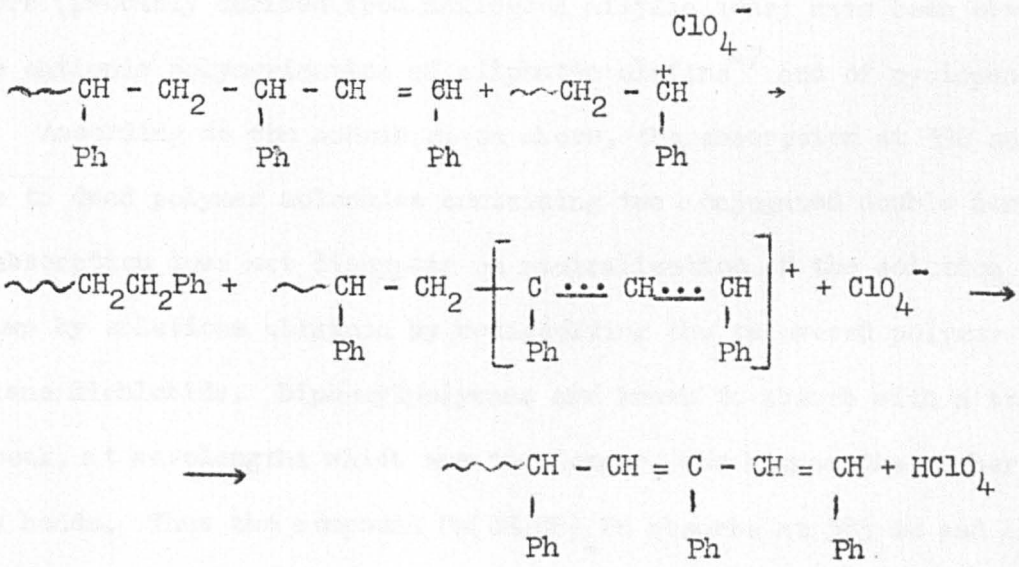
Run No.	$[st]_o$ (10^2M)	$[HClO_4]_o$ (10^4M)	$[H_2O]$ (10^4M)	t' (sec)	R_m^+ (10^5 mol^{-1} min^{-1})	$[P_n^P]_m$ (10^5M)
SGU8	7.1	6.3	-	475	0.725	5.96
SGU17	7.5	6.3	32.0	-	none	none
SGU9	18.0	18.0	-	180	11.09	37.6
SGU20	20.0	17.0	7.4	240	7.17	29.5

3.5.4 The reactions following the formation of polystyryl ions.

The position of the broad peak which slowly replaces the polystyryl peak (see 3.1.1), has been found to be variable, according to the polymer chain concentration in the reaction mixture. Thus for the Run SGU11, in which three successive additions of styrene were made (Table 14), the peak's λ_{max} was 450 - 453 mμ at the end of the first reaction, 462 - 463 mμ at the end of the second and 475 - 479 mμ at the end of the third.

The twin peaks appearing slowly in the spectra of the solutions, while the broad peak at 450 - 479 mμ diminished in intensity, were always at 390 mμ and 410 mμ.

The broad peak at long wavelengths is almost certainly to be attributed to allylic carbonium ions formed by hydride ion abstraction from an unsaturated polymer molecule, by a polystyryl ion. Proton transfer then produces a polymer with the two conjugated double bonds.



The bathochromic shifts of the absorption maxima with increasing chain concentration are compatible with the above mechanism, since an increase in the concentration of unsaturated chains will favour hydride abstraction and will therefore give allylic ions with higher degress of conjugation, which will absorb at wavelengths longer than 450 mμ.

A study of allylic-type carbonium ions[17] closely similar to those present in my system has been recently published. The ion $[Ph.CH\underline{\cdot\cdot\cdot}CH\underline{\cdot\cdot\cdot}CH.Ph]^+$ in CH_2Cl_2 solution was reported to absorb at 485 mμ at 20°.

Also, Szwarc[18] has shown that the polystyryl di-anion tends to produce similar types of ions, and ultimately polymers containing "internal" double bonds, by a process which is strictly analogous to the one I have postulated.

It is the first time that this kind of phenomenon is observed in a "cationic" polymerisation of styrene, although similar polyunsaturated polymers (probably derived from analogous allylic ions) have been obtained in the cationic polymerisation of aliphatic olefins[47] and of cyclopentadiene.[19]

According to the scheme given above, the absorption at 390 and 410 mμ is due to dead polymer molecules containing two conjugated double bonds. This absorption does not disappear on neutralisation of the solution and is shown by solutions obtained by redissolving the recovered polymer in methylene dichloride. Diphenylpolyenes are known to absorb with a strong twin peak, at wavelengths which are the longer, the higher the number of double bonds. Thus the compound $Ph(CH{=}CH)_4Ph$ absorbs at 385 mμ and 405 mμ.

The polystyrenes under consideration have a similar structure but possess the additional degree of conjugation offered by the presence of one phenyl group attached to every second carbon atom; this is why I have given the figures of two for the number of conjugated double bonds present in these polymers.

The concentration of these pairs of conjugated double bonds can be estimated by taking the extinction coefficients of the peaks shown by the diphenylpolyenes, for the calculations. Thus in the Run SGU11 the final concentration of these groups was about 25 per million polystyrene chains of $\overline{DP}$ about 5. Similar figures were obtained for other runs (10 - 25 pairs of conjugated double bonds per million polymer molecules).

Despite the very small proportion of these groups, they impart to the polymer solutions a very strong fluorescence. This, however, slowly disappears if the solutions are left open in the light, because of oxidation of the double bonds.

The concentration of allylic-type ions was presumably of the same order of magnitude as that of the resulting pairs of conjugated double bonds. However, since the extinction coefficient of such ions is probably as high as $\approx 10^5$, i.e. ≈ 20 times higher than that of the polystyryl ion, the resulting $D_{450-480}$ was of the same order of magnitude as D_{424}.

3.5.5 The effect of further monomer additions.

No matter at which stage after the end of the polymerisation of the first portion of styrene (i.e. after the induction period t'), addition of a further quantity of monomer induces complete decoloration of the solution (except for the fluorescence given by the polyunsaturated dead polymer molecules, see preceeding Section), with a corresponding reduction in conductivity. After a second induction period, during which the monomer is polymerised, colour and conductivity begin to reappear and the formation of polystyryl ions follow a pattern similar to that encountered at the end of the first polymerisation: this cycle can be repeated several times.

Fig. 37 illustrates these phenomena for a conductivity run in which four additions of styrene were performed. As can be seen in this Figure, when more styrene is added, the equivalent conductance (referred to the total perchloric acid concentration), does not go back to its original value during the first induction period, but to a somewhat higher one. However, this is not because a certain number of carbonium ions remain in solution after the addition, but because the free acid present after the end of the polymerisation is involved in side reactions, which slowly build up a small but noticeable concentration of ions. This has been confirmed in a run in which I crushed a phial of perchloric acid in methylene dichloride and thereafter took conductivity readings over a few hours. The acid concentration was 1.0×10^{-3} M, i.e. of the same order of magnitude as that used for the conductivity runs with styrene; a slow,

linear rise in conductivity was obtained, which indicated that ions were being formed by reaction of the acid with impurities in the system, most probably abstracted from the glass walls of the cell. The dotted line in Fig. 37 illustrates the results of this blank experiment.

Table 15 gives details for the experiment illustrated in Fig. 37.

Similar features were obtained in spectroscopic experiments involving further styrene additions; Table 14 refers to one of these; the plot of D_{424} against time was strictly equivalent to that shown in Fig. 37.

These findings (see also the run SGP11, for the equivalent in calorimetry) can be interpreted on the basis of the mechanism postulated in Section 3.5.3.

When free monomer is added to the solution containing polystyryl ions, equilibrium (12) is virtually destroyed, since total consumption of the free acid by the added styrene occurs; ester molecules are formed and stabilised by the excess of free monomer. In consequence of this reaction, equilibrium (14) is also drastically shifted to the left by the disappearence of free acid and thus the carbonium ions are removed from the solution. The effect of these phenomena is the disappearance of colour and the strong reduction in electrical conductivity.

A second induction period t'_2 follows the second styrene addition, its length being related to the amount of styrene added and to the new acid concentration by the relationships discussed in section 3.5.2.

The same applies to any further additions.

The amount of ions with respect to the acid concentration (Fig. 37

and Tables 14 and 15) becomes more important after each addition because of the increasing double bond concentration, as the polymer concentration increases. Thus the final value of the equivalent conductance and of D_{424} (or $D_{450-480}$) is higher after each addition, and will depend upon the actual concentrations of double bonds and of acid, as shown by equilibria (12) and (14).

Fig. 3B

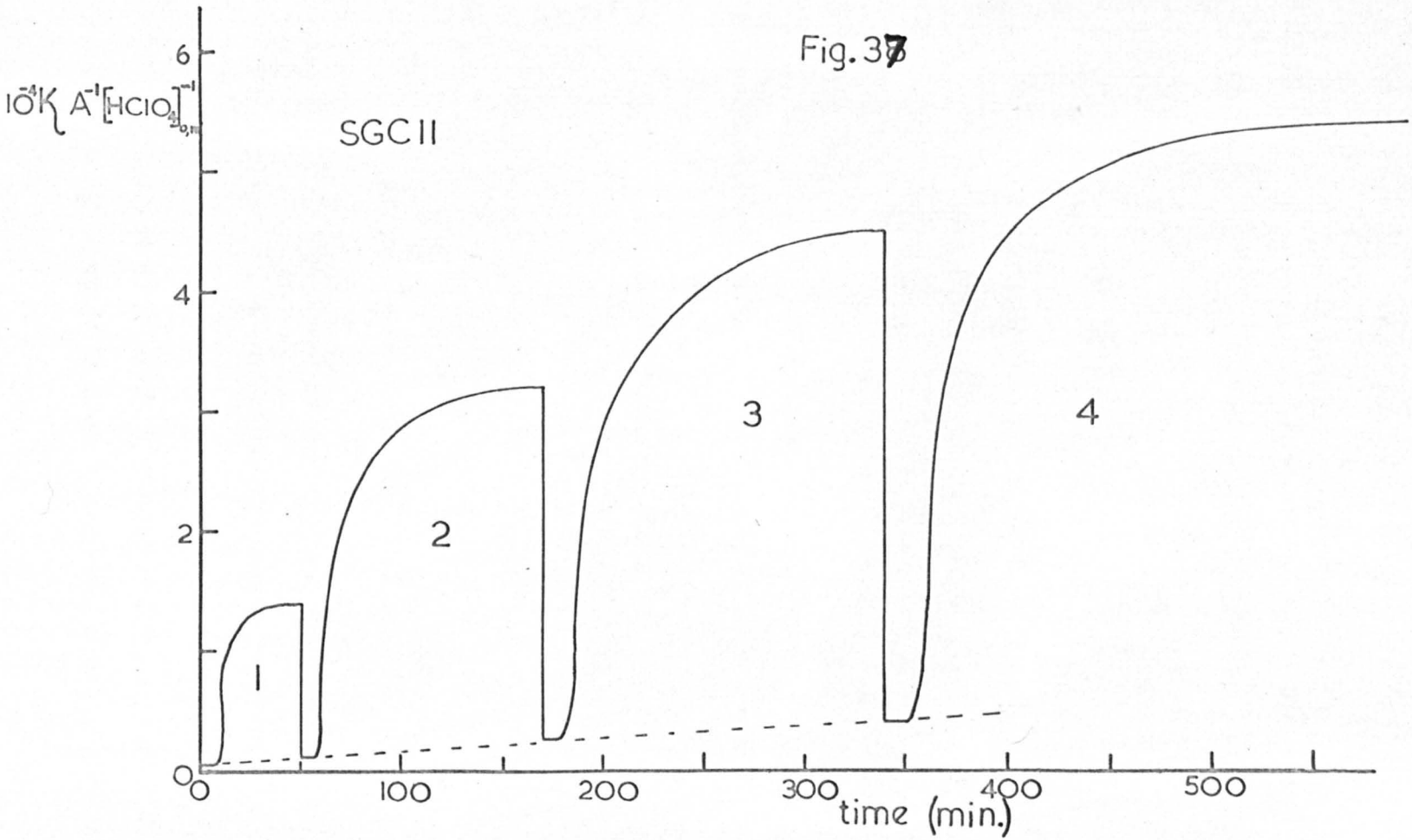

$10^4 K\ A^{-1}[HClO_4]_{0,m}^{-1}$
SGC II
6
4
2
0
0
100
200
300
400
500
time (min.)
1
2
3
4

Table 14

The effect of successive styrene additions on the spectroscopic behaviour of the system $HClO_4$ - styrene - CH_2Cl_2.

RUN SGU11

Addition (m)	$10^2[st]_{o,m}$	$10^4[HClO_4]_{o,m}$	t'_m (sec)	$[D_{450-480}]_{max}$	$[D_{410}]_{max}$
1	34.0	12.0	450	1.1 (452 mμ)	0.25
2*	37.9	11.8	480	1.3 (462 mμ)	0.41
3**	35.5	11.4	470	1.4 (477 mμ)	0.64

* 30 hours after beginning

** 50 hours after beginning

N.B. $D_{450-480}$ goes to 0 after each addition.

Table 15

The effect of successive styrene additions on the conductimetric behaviour of the system $HClO_4$ - styrene - CH_2Cl_2. (See Fig. 3[illegible], opposite).

RUN SGC11

Addition (m)	$10^2[st]_{o,m}$	$10^4[HClO_4]_{o,m}$	t'_m (sec)	K_A^{-1} (μMho)
1	6.1	8.0	320	11.13
2	8.3	6.67	450	20.8
3	10.6	5.24	700	23.4
4	13.5	3.75	1000	20.9

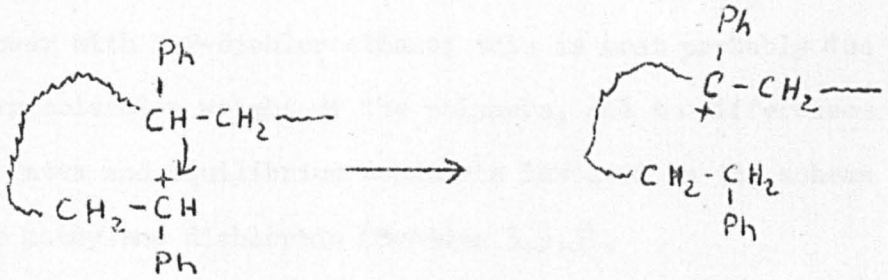
3.6 Interpretation of the results obtained with other solvents.

3.6.1 1,2-dichloroethane.

I did not proceed to a quantitative, systematic exploration of this system because the results obtained from the few spectroscopic runs indicated very clearly that the behaviour closely resembled that encountered when working with methylene dichloride.

The fact that the induction times were shorter than in methylene dichloride is readily explained by the fact that the polymerisation in 1,2-dichloroethane is faster, for the same working conditions.[7]

The only substantial difference between the behaviour in the two solvents, is the absence of secondary polystyryl ions in runs conducted in 1,2-dichloroethane. The ions produced at the end of the polymerisations are in fact tertiary carbonium ions; the reaction leading to the formation of these ions can be written as follows:



Whether this reaction takes place immediately after the end of the polymerisation, when the ester molecules start producing ions, or whether it is a true charge rearrangement occurring after secondary carbonium ions have been formed, is difficult to say, but the first hypothesis seems more likely, since I was never able to detect a peak at 424 mμ (secondary polystyryl ion) in the spectra relating to the present system.

The higher degree of polymerisation obtained when working with this solvent ($\overline{DP}$ = 7 - 9 at room temperature) is probably the main reason for this hydride abstraction taking place; the longer chains can in fact coil to a greater extent and thus the possibility of complete bending is reached here but not in the system involving methylene dichloride ($\overline{DP}$ = 5 at room temperature).

The formation of ions after the polymerisation followed in these runs a path strictly analogous to that given by equivalent runs in methylene dichloride. The final optical densities (D_{395}) were however always lower with 1,2-dichloroethane; this is most probably due again to the higher molecular weight of the polymers, and to differences in the reaction rates and equilibrium constants involved in the scheme already given for methylene dichloride (Section 3.5.3).

On the basis of these findings and of those reported by Pepper and Reilly[7] one can conclude that the polymerisation of styrene, catalysed by perchloric acid, in 1,2-dichloroethane, involves the formation of

ester molecules (1-phenylethyl perchlorate) which are the only chain carriers present in the system; both the kinetics of the polymerisation reactions and the phenomena following the monomer consumption, closely resemble those reported for methylene dichloride, with the exception of what has been described above.

3.6.2 Nitroalkanes.

The reasons for the peculiar behaviour of systems involving pure nitroalkanes or mixtures of nitroalkanes and chloroalkanes as solvent are obscure to me.

These solvents were used in an attempt to find a system which, because of the high polarity of the medium would display a pure cationic polymerisation.

The experiments in nitromethane showed that the polymerisation was very fast, but apparently proceeded in absence of carbonium ions. I thought however that no definite conclusions could be drawn from those runs, since the polymer had precipitated out of solution, and it was therefore unlikely that it could produce carbonium ions after the polymerisation. The runs in nitroethane have nevertheless confirmed that no carbonium ions are formed either during or after the polymerisation; and in this case the polymer was entirely soluble in the polymerisation medium.

It seems possible that the actual chain carrier is formed from the interaction of the nitroalkane with perchloric acid; this acid sequestration by the solvent does not seem however to involve the actual

destruction of the perchloric acid, since tests for chloride ions, at the end of the polymerisation runs were always negative. On the other hand the conductitivity of the final solutions was always rather high, much higher than at the end of runs in methylene dichloride; this indicates that ionic species are present in solution. I find it impossible, on the basis of the very little knowledge I have assembled on these systems, to formulate a reasonable interpretation which has to explain a rapid polymerisation promoted by chain carriers which are not carbonium ions, and which do not give carbonium ions at the end of the polymerisation.

Also obscure is the strong depression in the rate of polymerisation in nitroethane-1,2-dichloroethane mixtures; in these solvent mixtures the rate was always much lower than in either pure solvent, in agreement with Reilly's findings with open system.[7] These observations are mainly responsible for the difficulty in formulating a chemical interpretation of the results.

4. The polymerisation catalysed by sulphuric acid.

The great novelty of the ester mechanism in the polymerisation of styrene catalysed by perchloric acid induced me to study other systems, in order to see whether they exhibited analogous features, and whether therefore more general conclusions on the nature of the ester-catalysed polymerisation of styrene could be drawn.

The experiments to be described in this and the following sections do not pretend to cover exhaustively the systems chosen, but were simply carried out with the precise aim of establishing to which extent the carbonium ion theory, advocated for all of them by different authors, could be verified by the use of the new techniques developed during the course of this work.

Pepper and his collaborators[20] have reported on the polymerisation of styrene in 1,2-dichloroethane, catalysed by sulphuric acid. The kinetics of this system were interpreted by assuming that, as in the case of perchloric acid, the protonation of styrene was fast and complete, but that, owing to an important unimolecular termination reaction, involving the polymeric ions, the polymerisation came to an end before all the monomer had been consumed. In other words, no stationary state was attained and the decay in the number of chain carriers followed a simple first order path. The values for all the reaction rate constants (propagation, spontaneous transfer, monomer transfer and termination) were obtained from the application of this kinetic scheme to the experimental results.

However, to use Pepper's own words, "it must be emphasized that none of these processes (i.e. the different reactions postulated) has been identified in the chemical sense - they are simply plausible mechanisms for the various kinetic steps".

For catalyst concentrations ranging from 8×10^{-4} M to 4×10^{-3} M the time required for the chain carriers to disappear completely was about 10 minutes. Since with my spectroscopic technique I could start the scanning 20-30 seconds after the mixing of the reactants, it was concluded that if polystyryl ions were formed, it would have been largely possible to "see" them in the visible spectra of the reacting solutions.

Both silica and pyrex cells were attached to the usual spectroscopic device, to conduct this work; all runs to be described were carried out at room temperature.

4.1 The runs in methylene dichloride.

In the first run of this series a 1.75×10^{-3} M solution of styrene was made to react with an excess of sulphuric acid (4.6×10^{-3} M); no carbonium ions were formed in this reaction, but the peak at 292 mμ, due to the styrene, decreased fairly rapidly and had disappeared after about 15 minutes; no new peak was formed below 320 mμ; the solution absorbed monotonically from this wavelength upwards (i.e. towards shorter wavelength), and no maximum could be detected because the spectrum was off scale from 285 mμ. It was however clear that the tail which was being scanned could not be accounted for solely by the absorption of the benzene rings of polystyrene, since in that case the spectrum would

have been completely on scale, with a peak at 262 mμ with $D_{262} \simeq 0.4$. Nor could this absorption be attributed to indane end groups in the alledged polymer, for I shculd have been able then to detect the typical peak at 274 mμ. In conclusion the interaction of styrene with sulphuric acid under these conditions destroyed the olefinic double bonds, and yielded a compound giving a strong absorption peak with $\lambda_{max} < 285$ mμ.

Through a break seal, 0.55 grams of styrene were added to this mixture; no styryl (polystyryl) ions were formed on mixing, nor within the following 30 minutes, during which time the solution remained perfectly colourless. The device was then opened and the solution evaporated to dryness after neutralisation; virtually no polymer could be recovered. The solution left in fact 0.01 g of residue.

In the second run, the concentrations were chosen so as to reproduce a typical polymerisation run under Pepper's conditions ($[H_2SO_4]_o = 2.0 \times 10^{-3}$ M, $[st]_o = 0.46$ M). Again no ions could be detected at any time after the mixing of the reactants. The device was opened after 15 minutes, the solution neutralised and all volatile substances removed at 50° in a vacuum oven. The residue consisted of about 0.05 g of polystyrene (i.e. about 10% yield).

This run was repeated under similar conditions and gave virtually the same results.

A run carried out with roughly the same concentrations ($[H_2SO_4]_o = 2.5 \times 10^{-3}$ M, $[st]_o = 1.13$ M), but with wet solvent (the device was opened to the air 30 minutes before starting the reaction)

did not produce any carbonium ions; virtually no polymer could be recovered.

N.B. In the runs performed under vacuum, I noticed that occasionally bright yellow spots developed on the glass fragments of the crushed acid phial immediately after the mixing.

A few runs were then carried out in test tubes, by adding a saturated solution of sulphuric acid in methylene dichloride ($[H_2SO_4]_o$ = 1.13×10^{-2} M) to different mixtures of styrene and methylene dichloride. Only when a large excess (in volume) of the acid solution was added to neat styrene a vigorous polymerisation was obtained; this gave total conversion to polymer; during the mixing, the solution turned pale yellow-brown and remained coloured for a few minutes after the polymerisation had finished. In the other runs, with less acid, limited yields (5-15%) were obtained in 15 minutes and no colour could be noticed during that time. The molecular weights of these polymers were all about 3500 (Pepper[20] and Tsuda[21] obtained analogous figures at 25° in 1,2-dichloroethane, and at 28° in CH_2Cl_2 respectively).

4.2 <u>The runs in 1,2-dichloroethane</u>.

Two runs were conducted in this solvent; the reacting solutions contained 10 - 20% by volume of methylene dichloride, coming from the acid solution, since phials containing H_2SO_4-CH_2Cl_2 solutions were used for these runs.

No carbonium ions were detected at any time within the 30 minutes following the mixing, after which time the devices were opened

and the polymers recovered.

In the first run($[H_2SO_4]_o$ = 2.2 x 10^{-3} M, $[st]_o$ = 0.49 M) a conversion of about 80% should have been obtained according to Pepper's results; only 13% of the monomer did in fact polymerise.

In the second run ($[H_2SO_4]_o$ = 9.1 x 10^{-4} M, $[st]_o$ = 0.44 M) 27% of the monomer polymerised as opposed to a conversion of about 60% found by Pepper.

4.3 Interpretation of the results.

Even with a moderate excess of acid, styrene is not protonated by sulphuric acid; it is however consumed under these conditions to give, most probably 1-phenylethyl sulphate. This is the only likely reaction taking place between the two compounds, since sulphonation would not be expected to proceed so quickly under these particular conditions.

The results obtained with both solvents certainly disprove Pepper's theory of carbonium ions being formed on mixing at a concentration equal to that of the sulphuric acid; if this had been the case, the initial optical density of the reacting solutions would have been as high as 4 - 8, i.e. the solutions would have turned very deep yellow-brown.

A tentative explanation of both Pepper's and my results is offered below.

The system is extremely sensitive to the actual mechanics of mixing of the reagents (see the odd internal disagreement of my two runs in 1,2-dichloroethane); if the catalyst solution is thoroughly mixed with the monomer one, only 1-phenylethyl sulphate is formed and this is not

a chain carrier. If on the other hand a fairly high local concentration of catalyst results from incomplete mixing, styryl ions in very small concentrations can be formed. These will polymerise styrene, but as diffusion takes place, the excess of monomer will progressively reduce the concentration of these ions to zero and the polymerisation will cease.

My run in an open system with a high acid concentration, in which a yellow colour was formed and persisted during the polymerisation, gave 100% conversion, and thus supports the above interpretation.

Also, this interpretation is consistent with the very rapid initial reaction,[20-21] since I have shown (Section 3.5.2) that styryl ions are very powerful chain carriers.

A recent report[21] on the polymerisation of styrene by sulphuric acid shows that at all the temperatures studied (28° - -70°) "styrene polymerised rapidly as soon as the sulphuric acid was added, and thereafter the yield did not increase so markedly", (thus the author). In these experments the acid was added neat, to form a solution-suspension with $[H_2SO_4]_o$ = 0.06 - 0.3 M. These observations agree well with my interpretation.

Another piece of evidence in favour of the present transient carbonium ion theory is the fact, noticed by Pepper,[20] Tsuda[21] and myself (run in wet solvent) that water poisons the polymerisation, a common feature of carbonium ion reactions (see Section 3.5.3).

It must be pointed out that the present explanation of the experimental results is after all very similar to that offered by Pepper,[20] from a qualitative standpoint. It disagrees with it on two fundamental

questions, viz.:

a) The number of carbonium ions formed on mixing is very small, and not equal to the sulphuric acid concentration. This invalidates Pepper's figures for the different reaction rate constants.

b) The termination reaction is not an intrinsic kinetic feature of the system, but rather a purely mechanical phenomenon.

I realise that no direct proof has been offered for my theory, but only circumstantial evidence. This system is, however, very awkward to study mainly because of the very limited solubility of the acid in chlorinated hydrocarbons (the polymerisation does not proceed in aromatic hydrocarbons[21]), but also because as already stressed, it gives very irreproducible results, which discourages a more systematic approach to it.

I tried to synthesise the 1-phenylethyl sulphate from 1-phenylethanol and HSO_3Cl, but the attempt failed (two experiments).

The yellow spots observed on the phial fragments indicate that some acid was probably adsorbed in occasional cavities of the glass and that the high local acidity promoted the <u>in situ</u> ionization of styrene.

5. The polymerisation catalysed by trifluoroacetic acid.

Very little or no polymer was formed when 0.2 - 1 M solutions of styrene were mixed with 1 - 5 x 10^{-2} M solutions of trifluoroacetic acid in methylene dichloride. The solutions remained colourless after the mixing, and no carbonium ions could be detected. These observations agree with published results.[22]

When a concentrated solution of styrene in CH_2Cl_2 (1 - 3 M) is added to an equivalent volume of pure trifluoroacetic acid, polymerisation occurs fairly rapidly, but again the solution did not develop any peak in the visible region of the spectrum during this time. With time, however, a peak at 424 mμ, which slowly was doubled by a strong peak at 460 mμ, developed in the polymerised solution. These peaks were entirely discharged by neutralisation with ethanol. About 50% of the polymer was found to have polymerised under these conditions.

On the basis of previous evidence[22] and of the present set of experiments, the following conclusions can be drawn.

a) Only 1-phenylethyl trifluoroacetate is formed when styrene is mixed with relatively small quantities of trifluoroacetic acid, because the polarity of the medium is not high enough to activate this ester to the state of chain carrier.

b) When the acid concentration is raised above a certain critical value, the ester becomes chain carrier and a mixture of polystyrene and 1-phenylethyl trifluoroacetate is thus formed.

c) The formation of polystyryl and subsequently of allylic ions from the mixture of ester, polymer and free acid, follows probably a pattern of reactions similar to that encountered when dealing with the system $HClO_4$ - styrene - CH_2Cl_2 (Sections 3.5.3 and 3.5.4).

6. The polymerisation catalysed by Lewis acids.

6.1 Titanium tetrachloride.

The polymerisation of styrene catalysed by $TiCl_4$ in CH_2Cl_2 has been extensively studied by Longworth and Panton.[23] The nature of the chain carriers in this system is obscure, although the above authors were inclined to interpret their rather complicated results by a carbonium ion mechanism, on the evidence that the polymerising solutions were always pale yellow.

The interaction of $TiCl_4$ ($3 \times 10^{-2} - 3 \times 10^{-3}$ M) with small quantities of styrene ($1 \times 10^{-3} - 1 \times 10^{-4}$ M) does not yield, under anhydrous conditions, any styryl ions. The visible spectra for these runs remained always completely blank. In the ultraviolet the absorption of free $TiCl_4$ precluded the possibility of scanning at wavelengths lower than about 330 mμ; between 330 mμ and 400 mμ the tail of a peak (probably due to the π-complex of the olefin with the metal halide) virtually occupied the whole of the scanning range.

Spectroscopic runs, carried out under typical polymerisation conditions ($[TiCl_4] = 10^{-3} - 10^{-2}$ M, $[st]_o = 0.2 - 1$ M) revealed the presence of a rather strong absorption in the region 350 - 500 mμ (off scale at lower wavelengths), produced by the tail of a peak with $\lambda_{max} < 340$. The intensity of this absorption band decreased by about a half of its initial value within the first 20 minutes, then remained constant for several hours. No sign of a peak or shoulder around 420 - 430 mμ could be noticed. Polymerisations went to 100% conversion.

The absorption in the visible region is therefore due to the tail of the strong π-complex peak; the decrease in its intensity reflects the consumption of monomer and consequent formation of a less strong complex between $TiCl_4$ and the phenyl groups[24] in the polymer.

Because of this interference, we could not safely conclude against or in favour of carbonium ions, since they might have been present in very small concentrations, and their peak thus completely masked by the main absorption band. It can only be concluded that the yellow colour noticed by Longworth and Panton in the polymerising solutions was mainly due to the π-complex between styrene and the catalyst.

6.2 Boron Fluoride.

The polymerisation of styrene catalysed by boron fluoride has received the attention of several researchers,[25] who have all postulated the presence of carbonium ions to explain the different reactions involved in their systems.

A phial containing 1 ml of a saturated solution of BF_3 in CH_2Cl_2 (BF_3 is only sparingly soluble in this medium), was crushed into a 0.5 M solution of styrene in the same solvent. Polymerisation was fast and probably complete within a few seconds. The visible spectra of the solution exhibited a peak at 420 mμ which increased in intensity during the first few minutes following the mixing, and then remained constant. The run was repeated and scanning at 420 mμ started 15 seconds after the mixing; D_{420} increased from 0.025 (after 15 seconds) to a constant value of 0.08 (after 15 minutes). A drop of ethanol discharged the peak

completely. Polymerisation was complete in both cases.

These runs will be discussed together with the polymerisations catalysed by stannic chloride, in the following section.

6.3 Stannic Chloride.

Colclough and Dainton[26] have reported on the kinetics of the polymerisation of styrene catalysed by stannic chloride in different solvents. Water is a cocatalyst in these systems, but so are some of the solvents themselves (chlorinated hydrocarbons). In a detailed and rather complex scheme of reactions these authors produced a chemical interpretation for their experimental results, entirely based on carbonium ions, allegedly formed by the interaction of the metal halide-cocatalyst addition compound with one or two molecules of styrene.

Many other researchers have investigated the action of $SnCl_4$ as catalyst for the polymerisation of styrene in the past thirty years or so; a very detailed review of these efforts has been recently written by Mathieson.[1]

Stannic chloride solutions in methylene dichloride absorb in the ultraviolet; a 1×10^{-2} M solution gave an absorption band monotonically decreasing in intensity from 255 mμ (off scale) to 285 mμ ($D_{285} = 0.008$). When styrene was added to this solution (through a break seal on the spectroscopic device) to give $[st]_o = 2.7 \times 10^{-3}$ M, no carbonium ions were formed, and only a very small fraction of the olefin (about 5%) was consumed within a few minutes from the mixing,

probably to give a π-complex with $SnCl_4$. A second addition of styrene was carried out to bring its concentration up to 2.7×10^{-2} M; again, no carbonium ions could be traced in the visible spectrum, but it was possible now to register an absorption band due to the π-complex. The maximum, obtained by subtracting from this spectrum a standard spectrum of styrene at the same concentration, was calculated to occur at 300 ± 5 mμ. The progressive decrease in the absorption band due to the complex could be accounted for by a slow polymerisation of the styrene. The π-complex formed by $SnCl_4$ with the benzene ring absorbs in fact at shorter wavelengths.[27] The device was opened several hours after the second styrene addition and the polymer was isolated in almost 100% yield.

Two more runs were carried out with similar styrene concentrations but with higher $SnCl_4$ concentrations (8.7×10^{-2} M and 0.24 M respectively). The formation and subsequent strong reduction of the absorption band due to the π-complex was very clear and more accurate measurements indicated that the corresponding maximum must be at 295 ± 3 mμ. Polymerisation of styrene proceeded to completion in a few hours, but no carbonium ions could be detected under these conditions during or after the polymerisation. Attempts to assess a value for the extinction coefficient of the peak due to the π-complex and the dissociation constant of this, failed because of the instability of the peak, which started decreasing strongly from the beginning, as the polymerisation proceeded.

Three runs were then conducted under typical polymerisation conditions ($[st]_o$ = 0.3 - 0.6 M, $[SnCl_4]$ = 0.1 - 0.3 M). Polymerisation proceeded in these runs fairly rapidly (it was followed through the decrease of the tail of the π-complex) and was complete in about an hour. During this time no absorption was recorded at wavelengths higher than 400 mμ. Several hours after the mixing, however, a broad, but small peak around 430 mμ was always formed, and the solutions acquired a pale but distinct yellow colour. The optical density of this peak ranged between 0.03 and 0.06. Neutralisation of the solution, after the device had been opened to the air, destroyed this peak completely.

Finally, one run was conducted to study the influence of added quantities of water to this system. The concentrations were $[SnCl_4]$ = 8.0×10^{-2} M, $[st]_o$ = 0.57 M, $[H_2O]$ = 5.0×10^{-3} M). Polymerisation was rather fast and reached completion in about 30 minutes; no absorption was recorded around or above 420 mμ during this time, but a broad peak slowly developed in the following few hours, while the solution turned pale yellow (D_{420} = 0.05).

The following conclusions have been drawn on the basis of the above results and of some published observations on similar systems.[6,27]

a) It has been reported[27] that styrene and $SnCl_4$ form in 1,2-dichloroethane a 1:1 complex absorbing in the ultraviolet (λ_{max} = 307 mμ); the technique employed by these authors is however, liable to strong criticism, since they used as reference

for the scanning of the spectra a styrene solution with concentration equal to the initial styrene concentration used in the reaction cell; styrene is consumed in the reaction cell both by the formation of complex molecules and by polymerisation (the work was conducted in an open system, so that polymerisation was certainly very important at the concentrations used). It is obvious that soon after mixing there will be a rather large difference in styrene concentration between the sample and the reference cells and the actual values of optical densities around 300 mμ will be too small, since the reference solution absorbs more strongly. Moreover, the shape of the peak due to the complex and its maximum will be strongly affected by these circumstances. In fact it can be seen from the published spectra that the peaks are not at all symmetrical, their short wavelength branch being much steeper than the other; this is due to the styrene in the reference cell absorbing in that particular section of the spectrum. The λ_{max} which these authors produced is therefore too high; our value of 295 $\pm$ 3 mμ supports this argument. But the most important consequence of this faulty approach lies in the calculations by which values of the propagation rate constant were derived; these values must now be regarded with great suspicion.

b) The absence of ions during the polymerisation of styrene catalysed by stannic chloride has been observed spectroscopically by other authors who worked under conditions very similar to mine, but in 1,2-dichloroethane.[28]

Jordan and Treloar[6] have reported that polystyryl ions are formed during the polymerisation of styrene (4.22×10^{-2} M) catalysed by $SnCl_4$ (0.174 M) in 1,2-dichloroethane. At first sight their results appear to be ir conflict with mine, but since they took the first spectrum 30 minutes after the mixing of the reactants, and since they were working in an open system, it might well be that by that time the actual polymerisation had finished and that they were therefore observing a phenomenon similar to that described in my report. Moreover, the spectrum published as evidence for their argument is rather unsatisfactory (very broad and small peak) and it is surprising that they could give a figure for the absorption maximum (410 mμ) for a peak which has the same optical density (≈ 0.06) between 400 and 425 mμ.

c) Under the conditions studied, the polymerisation of styrene catalysed by $SnCl_4$ does not seem to proceed through a carbonium ion mechanism, unless of course, a very small amount of styryl ions, undetectable by our spectroscopic technique, was responsible for the consumption of the monomer; but if this had been the case, the addition of water, which enhances the rate of polymerisation should have sensibly increased the ionic concentration, and I would have been able then to "see" the styryl ions.

d) A small quantity of carbonium ions (most probably polystyryl ions) is produced at the end of the polymerisation reaction. This reflects a situation already encountered during the course of this work (sections 3.5.3 and 5).

e) There is some evidence for postulating for the present system an ester mechanism involving a small concentration of a compound formed by the reaction illustrated below, the population of which would depend upon the water concentration for $[H_2O] < [SnCl_4]$.

$$SnCl_3OH + CH_2{:}CHPh \rightarrow Cl_3Sn\text{-}O\text{-}\underset{\displaystyle Ph}{\underset{|}{CH}}\text{-}CH_3$$

But other protonic acids derived from $SnCl_4$ and H_2O might also be involved.

The results obtained with the system BF_3 - styrene - CH_2Cl_2 are more difficult to interpret, for the polymerisation reaction is too fast, and I do not know whether the ions are actually present <u>during</u> the propagation, or whether they are formed immediately after the end of it. The only supporting piece of evidence in favour of the second hypothesis is the fact that the polystyryl ion concentration increased considerably during the first few minutes of scanning, but this is not conclusive, because D_{420} was not zero when I started the scanning.

PART II : ACENAPHTHYLENE

7. Introduction.

The logical extension of my search for an ester catalysed reaction (or, on the other hand, for a clear and cut true cationic system) consisted in studying other monomers.

There are few studies on the "cationic" polymerisation of acenaphthylene; the only publication dealing with the kinetic aspects[29] has raised considerable suspicions, since other researchers have not been able to reproduce either the kinetics or the degrees of polymerisation reported.[30]

The main reason for my choosing this monomer was that its visible spectrum exhibits a peak with very low extinction coefficient (Spectrum 1), which is not exhibited by the polymer and could therefore be used as a means of following the disappearance of monomer during the polymerisation, even at fairly high monomer concentrations. It was hoped thus to follow both the kinetics and the carbonium ion concentration during the same run, by using the customary spectroscopic technique.

8. The proton adduct of acenaphthylene.

The interaction of an excess of perchloric acid with acenaphthylene (AN) was studied under conditions similar to those employed in the protonation of styrene (Section 2). The system was, however, found to be very unstable, and the carbonium ions formed were rapidly destroyed by important side reactions. Two peaks in the visible region of the spectrum were formed on mixing, at about 420 mμ and 640 mμ. Their optical density decreased rapidly with time, while a strong broad band at about 450 mμ and a new peak at 570 mμ replaced them. If the excess of acid was reduced (down to ratios [acid]/[AN] of 5), an important quantity of the olefin was dimerised, and computation of the ionic concentration became virtually impossible. Only approximate values of the extinction coefficients were therefore obtained for the two visible peaks, viz. $\varepsilon_{420} \approx 2 \times 10^3$ and $\varepsilon_{640} \approx 4 \times 10^3$. The ultraviolet spectrum of the carbonium ion was even more difficult to obtain, because small traces of AN dimer formed on mixing would "cover" a great part of this region (see Spectrum 2). This system was abandoned after 6 runs.

The protonation of AN dimer under similar conditions proved just as intractable, and was left after two runs. Peaks at 420 mμ and 640 mμ were obtained for the resulting carbonium ion, but both extinction coefficients were about double those calculated for the monomer ion.

The protonation of AN in concentrated sulphuric acid proved to give much more satisfactory results. Standard solutions of the olefin were made up in glacial acetic acid and these were treated with a large excess of 98% AnalaR sulphuric acid.[2,5] The details of these operations have been described in Chapter Three.

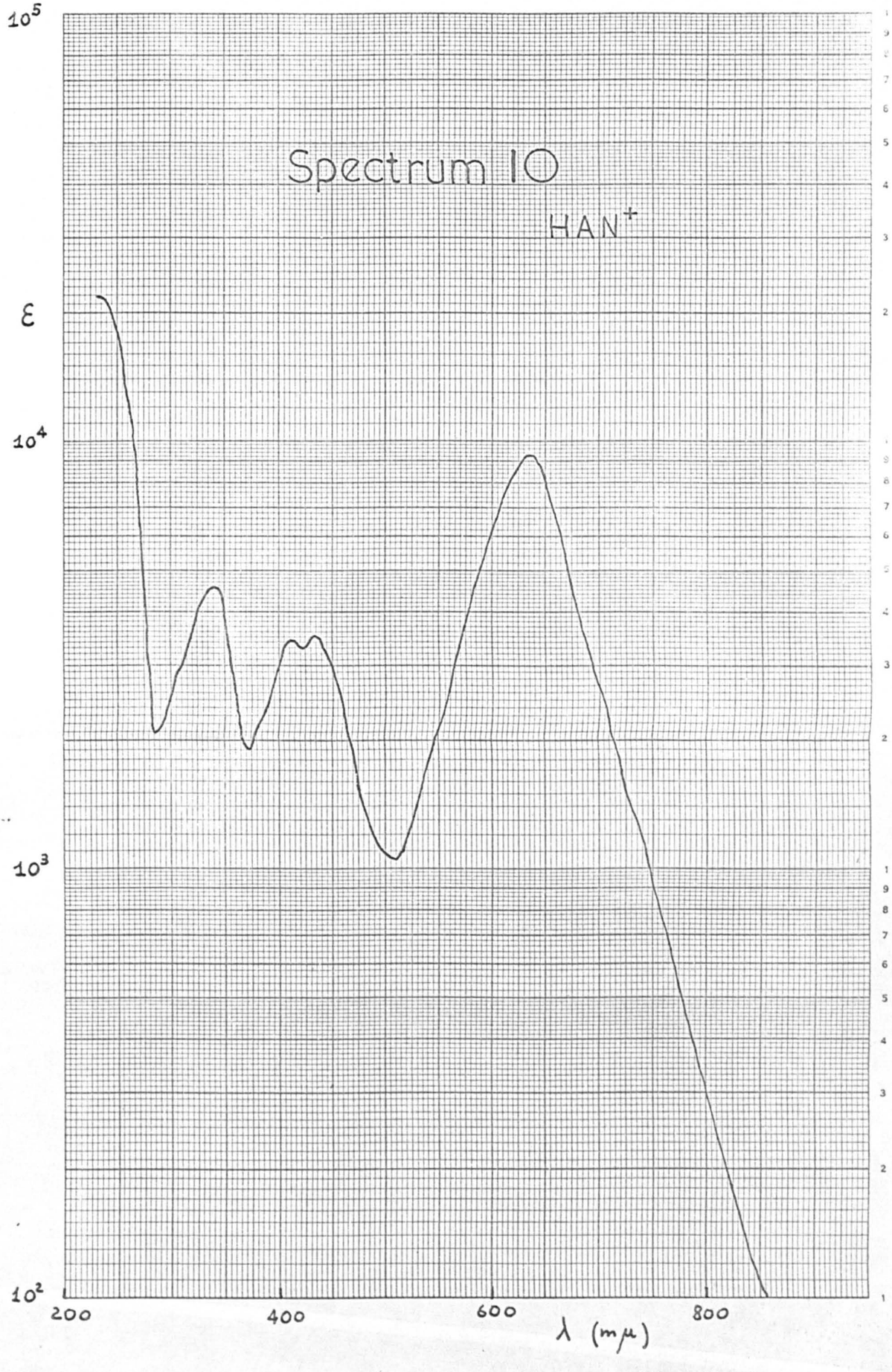


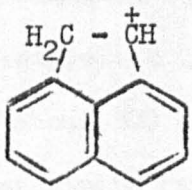
Table 16

Data on the protonation of AN by pure H_2SO_4

Run No.	10^4[AN]	D_{341}	D_{410}	D_{431}	D_{640}
AGU10	0.61	0.24	0.17	0.175	0.55
AGU9	1.02	0.44	0.33	0.34	0.95
AGU8	1.97	0.90	0.72	0.74	1.80

Spectrum 10 (Opposite)

The ultraviolet and visible spectrum of the acenaphthylcarbonium ion in methylene dichloride.



λ_{max}(mμ)	$10^{-3}\varepsilon$
341	4.57
410	3.40
431	3.50
640 ± 4	9.20

Stable green-yellow solutions were obtained, which exhibited exactly the same spectrum for at least 30 minutes. Good Lambert-Beer plots were obtained for all D_{max}'s indicating that protonation had gone to completion in all runs ([AN] = 6×10^{-5} - 2×10^{-4} M). No dimer was formed under these conditions.

Spectrum 10 and Table 16 illustrate the results obtained. The values of the extinction coefficients suggest that secondary reactions destroying ions had been very important in the protonation of AN by perchloric acid, while a better situation in this sense had been attained in the protonation of the dimer.

N.B. The standard deviation in λ_{max} for the long wavelength peak is rather high because the UNICAM SP 700 instrument records in wave numbers and therefore that part of the spectrum, when converted into wavelengths, becomes very compressed.

The high degree of conjugation of the AN carbonium ion (see below), can explain the displacement of the two peaks (which for phenyl-type carbonium ions are at abour 300 and 430 mμ respectively) towards longer wavelengths; the approximate ratio of 1:2 for the ratio $\varepsilon_{410-430} / \varepsilon_{640}$ is however maintained (see Section 2.2). A similar bathochromic shift was obtained by Gold and Tye[2] for the carbonium ion derived from α-naphthyl-1-phenylethylene, which also gave rise to a third peak, in addition to the two "usual" ones at shorter wavelengths.

For the spectroscopic study of polymerisations to be described, it was assumed that the AN carbonium ion would have in CH_2Cl_2 the same spectral characteristics as in sulphuric acid.

9. The polymerisation catalysed by perchloric acid.

The kinetic feautres of the polymerisation of AN catalysed by perchloric acid seemed rather complicated, according to the results obtained from a few orientation runs conducted at 25° in methylene dichloride in an open system. Time-conversion curves were obtained by sampling known volumes of the reaction solutions, quenching the samples in ethanol, and recovering the precipitated polymers. The over-all order of the polymerisations was 2.5, but the initial rate of polymerisation was proportional to the first power of the acid concentration. However, too few runs were carried out for a clear-cut picture to be obtained. During the polymerisations it was noticed that the solutions became greenish, while the initial deep yellow colour of the solutions faded as the monomer was consumed. It was therefore decided to study the behaviour of this system by spectroscopy, since, as mentioned earlier, this technique would offer the opportunity of following the rate of monomer consumption (peak at 465 mμ) together with the changes in carbonium ion concentration (peak at 640 mμ).

Two runs were carried out at room temperature, with the following concentrations: $[AN] = 1.2 \times 10^{-2}$ and 1.0×10^{-1} M respectively and $[HClO_4] = 2.37 \times 10^{-4}$ in both runs.

Small proportions of AN dimer were formed in both experiments (and indeed in all other preliminary runs I conducted with this catalyst) and these made it impossible to follow quantitatively the disappearance of monomer, since they imparted to the solutions a strong fluorescence with a corresponding absorption which tailed up to 450 - 460 mμ (see Spectrum 2). The following important observations could however be

recorded:

a) In the run with the lower [AN], a considerable amount of carbonium ions were formed on mixing and their concentration increased during the first 4 minutes (peak at 655 ± 4 mμ, D_{655} increasing from 0.2 to 0.6 in 4 minutes). This roughly corresponded to the polymerisation period (comparison with kinetic results from open systems); D_{655} then decreased slowly, and a new peak at 572 ± 2 mμ grew correspondingly. After 5 hours only the peak at 572 mμ was left in the visible spectrum (in addition to the tail of the dimer peak, and a shoulder at about 475 mμ). The device was opened and the polymer was reocvered in 100% yield.

b) In the second run with a tenfold increase in monomer concentration, a very small peak at 655 mμ formed on mixing ($D_{655} \approx 0.05$), but the solution exhibited a broad absorption band starting as a shoulder on the tail of the dimer peak at about 500 mμ and extending up to about 800 mμ. The peak at 655 mμ disappeared slowly within about 30 minutes, and only the broad band was left in the visible region. Several hours later, however, a peak at 572 mμ had also appeared.

Polymerisation was complete under these conditions.

The system was abandoned because it proved to be too complicated to make further efforts worthwhile. The above results will be discussed in conjunction with those relating to the runs conducted with sulphuric acid as catalyst.

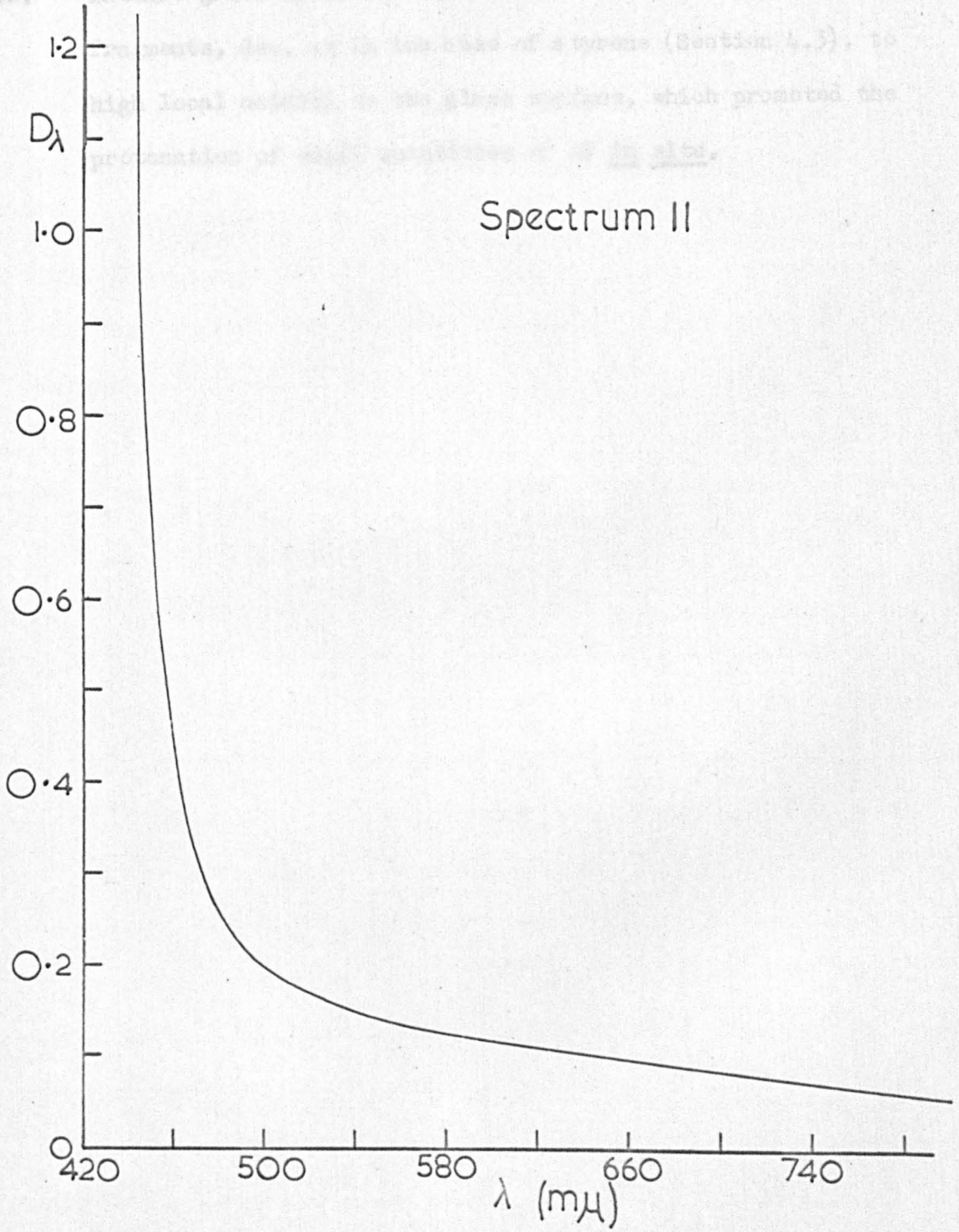
10. The polymerisation catalysed by sulphuric acid.

Two runs were carried out with the usual spectroscopic device at room temperature, in methylene dichloride.

The concentrations of the reactants were [AN] = 0.105 M and $[H_2SO_4] = 9.78 \times 10^{-4}$ M in the first run and [AN] = 0.080 M and $[H_2SO_4] = 2.83 \times 10^{-3}$ M in the second.

In both experiments polymerisation proceeded without appreciable formation of dimer (at least in the first part of the reaction). The mixing of the reactants did not lead to the formation of carbonium ions, but in both runs a broad absorption band (about twice as intense in the second run as in the first) was exhibited by the visible spectra of the polymerising (and polymerised) solutions. Spectrum 11, one of those taken after the end of the polymerisation in the second run, shows this absorption band, which closely resembled that obtained with perchloric acid.

Spectrum 11 shows that the solutions did absorb around 650 mμ, but the assertion that no carbonium ions were present during these runs is substantiated by the fact that the spectra obtained after opening the device and neutralizing the solutions with a few drops of ethanol, were virtually identical to Spectrum 11, thus proving that the absorption around 650 mμ was uniquely due to the tail of the unidentified band, and not to AN carbonium ion. Polymerisations were rather slow; e.g. in the second run it took about 3 hours for the monomer to be completely consumed.


Spectrum II
1·2
D_λ
1·0
0·8
0·6
0·4
0·2
0
420
500
580
660
740
λ (mμ)

N.B. Intense green spots were noticed on some of the phial fragments, due, as in the case of styrene (Section 4.3), to high local acidity on the glass surface, which promoted the protonation of small quantities of AN *in situ*.

11. Interpretation of the polymerisation results.

The conclusions I have drawn from these few experiments can be summarised as follows:

a) As in the case of styrene a bathochromic shift of minor importance occurs in the visible peak of the monomer carbonium ion, when this is replaced by the polymer ion. In the present system the AN proton adduct absorbs at $\lambda_{max} = 640 \pm 4$ mμ and the polyacenaphthylene carbonium ion at $\lambda_{max} = 655 \pm 4$ mμ. The peak at 570 ± 2 mμ formed from the AN carbonium ion in a degradation reaction, in polymerisations involving perchloric acid (Sections 8 and 9), is probably due to the formation of a radical ion, similar to that postulated for triphenylethylene, in Chapter Three.

b) The polymerisation of AN catalysed by perchloric acid is relatively fast and carbonium ions are present during the monomer consumption. It seems therefore plausible to conclude that the ions are the chain carriers in this system (or one of the chain carriers). The ionic concentration decreases, however, as the AN concentration increases, for the same $[HClO_4]$; moreover the carbonium ion concentration increases during a given polymerisation, as the monomer is consumed. Even at the lower initial monomer concentration, the maximum number of AN carbonium ions obtained was about 1/4 of the acid concentration, indicating that not all the catalyst protonated the monomer, even under the most "favourable" conditions.

All these observations, together with the fact that another species is present in polymerising solutions (that giving rise to

the broad absorbtion band in the visible spectrum), seems to indicate that the reaction between $HClO_4$ and AN produces a mixture of carbonium ions and ester molecules and that the relative population of these two speies strongly depends on the excess of olefin present during the reaction. The more olefin, the higher is the ratio [ester]/[ions], as in the case of styrene (Section 3), because the excess of monomer stabilises the ester. The fact that some carbonium ions are formed from the beginning of the reaction, is likely to be attributed to the higher basicity of AN, compared with styrene, which would enhance to tendency to form ionic species in equilibrium with ester molecules.

c) When perchloric acid is replaced by the weaker sulphuric acid, no ions are formed, and the ester acts as chain carriers; the rates of polymerisation were much lower in this system, in general agreement with the fact that the ester molecules are much less effective chain carriers than the corresponding carbonium ions. I am inclined to attribute the broad absorption band, shown in Spectrum 11 (this shows in fact the tail of the true ester peak) to the ester molecules, although I cannot offer at present any proof for this.

These conclusions have a very preliminary character and it is obvious that each of the two systems requires a great deal more study, before a definite interpretation of the reaction mechanisms involved can be put forward.

PART III : N-VINYLCARBAZOLE

12. Introduction.

N-vinylcarbazole (NVC) is one of the most basic monomers known, and it polymerises readily even in presence of very weak acids such as acetic acid (see below). Recent reports on the polymerisation of this monomer catalysed by nitroalkanes and nitrobenzene[31] and by carbon tetrahalides,[32,33] must be mentioned here, for, like all other publications on the acid and Lewis acid catalysed polymerisation of NVC,[34] they advocate a carbonium ion mechanism to explain the chemistry of the reactions. No thorough kinetic study of a given "cationic" polymerisation involving NVC is to be found in the literature, except for a study of the system NVC - $MgClO_4$ - ethylacetate by Solomon.[35] On the basis of my findings, (see below), it seems very likely that the true catalytic agent was in that case nothing but traces of perchloric acid, originated from partial hydrolysis of the magnesium perchlorate.

My choice of this monomer was dictated by the hope of obtaining a purely cationic system, where, because of the extraordinary basicity of the monomer, carbonium ions would be the only species produced by its reaction of the catalyst (especially with perchloric acid).

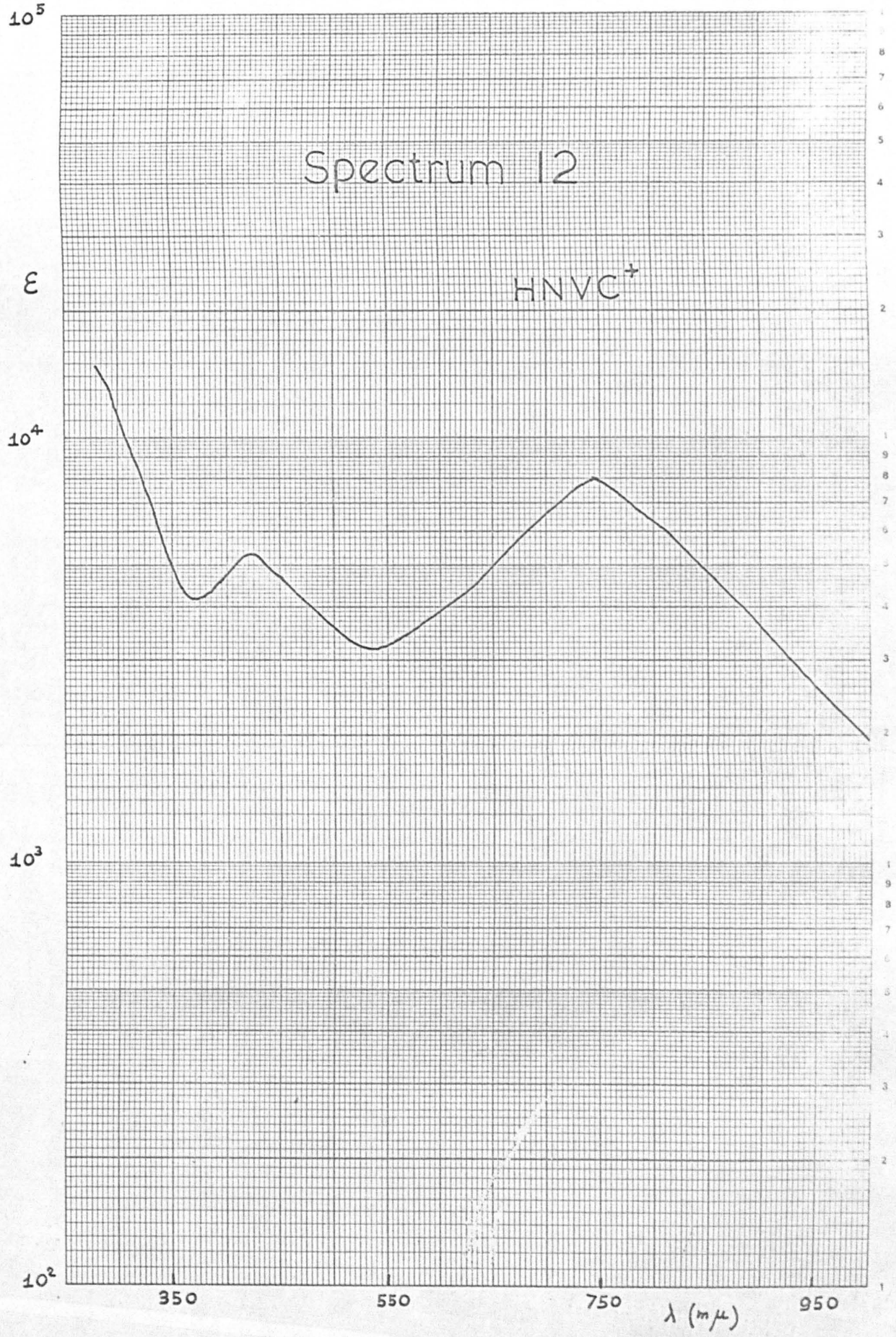

Spectrum 12
HNVC+
ε
10^5
10^4
10^3
10^2
350
550
750
950
λ (mμ)
LOG 3 CYCLES X MM. & 1 CM.
GRAPH SHEET No. 5531

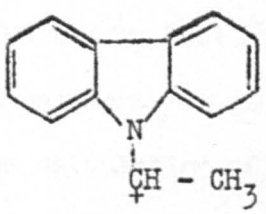
Table 17

Data on the protonation of NVC by $HClO_4$ in CH_2Cl_2

Run No.	10^4[NVC]	10^2[$HClO_4$]	D_{420}	D_{764}
VGU7	0.61	2.43	0 33	0.50
VGU2	0.72	1.24	0.37	0.62
VGU5	0.82	1.77	0.42	0.67
VGU8	3.18	3.00	1.70	2.50

Spectrum 12 (Opposite)

The ultraviolet and visible spectrum of the protonated N-vinylcarbazole in methylene dichloride.



λ_{max}(mμ)	$10^{-3}\varepsilon$
417-425	5.3
746 ± 4	8.0

13. The protonation of NVC.

NVC does not dissolve in 98% sulphuric acid; the crystals of monomer cover themselves with a dark brown coating, when mixed with this compound. In an attempt to obtain the NVC carbonium ion by the standard technique involving the preparation of acetic acid solutions of the olefin,[2] I discovered that NVC polymerises when dissolved in glacial acetic acid. The polymerising solutions are perfectly colourless and complete conversion is attained at room temperature in about 30 minutes.

Seven runs were carried out in the usual spectroscopic device (silica cells) in order to obtain the spectrum of the NVC carbonium ion in methylene dichloride, by the reaction of an excess of $HClO_4$ with the olefin. It was noticed that only when mixing was very fast and thorough (small working volume, and good crushing of the phial) and when the ratio $[HClO_4]/[NVC]$ was very high (150 - 400), all the olefin was protonated; polymerisation of NVC was in fact so fast under these circumstances, that if the above conditions were not met, a sensible amount of polymer was formed, and thus the calculation of the extinction coefficients became impossible. Four of the seven runs gave acceptable results. The spectrum of the NVC carbonium ion was fairly stable; side reactions did occur, but they were relatively slow. Spectrum 12 and Table 17 illustrate the present findings; the values of the extinction coefficients were obtained for the two absorption maxima, from good Lambert-Beer plots obtained from the four satisfactory runs given in the table. As will be shown below, Spectrum 12 is in fact that of the NVC carbonium ion and not that of the quaternary ammonium perchlorate.

14. The polymerisation catalysed by perchloric acid.

Three polymerisation runs were carried out in the adiabatic calorimeter, using CH_2Cl_2 as solvent, at 15°. The NVC was placed in the vessel, whilst the acid and the water were added by crushing phials. The Table below gives the concentrations used for these runs:

Run No.	[NVC] (M)	[$HClO_4$] (10^4M)	[H_2O] (10^4M)	$\bar{M}_n$*	$[\eta]$***
VGP1	0.112	6.86	-	32000	0.25
VGP2	0.126	0.435	-	48000	0.39
VGP3	0.120	0.61	2.45	36000	0.32

*Determined by vapour pressure osmometry (See Chapter 1).

***in benzene at 25°.

In the three experiments the polymerisation was completed within one or two seconds, i.e. the reaction trace was virtually perpendicular to the time axis, despite the high speed employed for the recorder chart (60 mm/minute). The polymerised solutions had a very pale blueish fluorescence. The polymers were recovered by precipitation with industrial ethanol: the fine, white powder was filtered, washed repeatedly with the precipitant and dried at 50° in a vacuum oven to constant weight. Conversions were 100% for all three runs.

Four runs were then carried out in the spectroscopic device with pyrex cells at room temperature in CH_2Cl_2, with the concentrations

shown in the Table below.

Run No.	$[HClO_4]$ (10^4M)	[NVC] (M)
VGU12	5.41	0.026
VGU11	5.40	0.052
VGU9	7.70	0.136
VGU10	23.4	0.148

Because of the high catalyst concentration, NVC carbonium ions were formed during Run VGU10 (D_{755} = 0.15, constant between 15 seconds and 10 minutes after mixing), but their concentration corresponded to a protonation conversion, based upon the initial acid concentration, of only 0.8%. As time passed the solution became deeper and deeper green; the spectra, frequently scanned, showed that the new peaks at 680 mμ and 435 mμ were slowly appearing, while the original carbonium ion peak at 755 ± 5 mμ had disappeared within about 1 hour from mixing.

The device was opened to the air two hours after mixing and the solution was treated with a few drops of ethanol; the colour was slowly discharged, and the visible spectrum exhibited then a monotonically decreasing absorption from 400 - 800 mμ ($D_{680 - 760} \approx 0.02$). The $\overline{DP}$ of the recovered polymer was about 160.

A very small number of carbonium ions could be "seen" at $\lambda = 755 \pm 5$mμ during the Run VGU12, roughly 0.3% of the perchloric acid

present, probably because of the relatively low monomer concentration. It was again noticed that increasingly strong peaks at 680 mμ and 435 mμ were in the visible spectra of the solution, as time passed; D_{680} and D_{435} increased slowly for as long as the solution was left under vacuum, the device being kep in the dark. When the device was opened, three days after the mixing, D_{680} was 0.54, and D_{435} about 1. These peaks were slowly discharged by addition of ethanol.

Runs VGU9 and VGU11 did not produce a detectable quantity of carbonium ions, but the two usual peaks in the visible spectra grew in a way similar to that described for Run VGU12. Again the spectrum of the solutions after treatment with a few drops of ethanol only exhibited an absorption band decreasing monotonically from 400 to 800 mμ. These spectra were very similar to those obtained for the system AN - H_2SO_4 - CH_2Cl_2, typified in Spectrum 11. The $\overline{DP}$ of the polyNVC obtained from Run VGU9 (the only run for which I had enough polymer for a determination) was around 150.

15. The polymerisation catalysed by sulphuric acid.

The system NVC -- H_2SO_4 - CH_2Cl_2 produced phenomena which were too fast to be studied by the present spectroscopic techniques.

In a typical run ($[H_2SO_4]$ = 8.30 x 10^{-4} M, [NVC] = 0.40 M) at room temperature, the solution turned intense yellow when the acid phial was crushed; this colour however, faded away very rapidly, being replaced by a fairly deep green colour; by the time the first spectrum could be taken, only a peak at 658 mμ could be detected; D_{658} then decreased rather quickly with time (half life of about 30 minutes). Addition of ethanol to the solution in the opened device destroyed this peak and the spectrum was the usual, described in the preceeding sections, and similar to that shown in Spectrum 11. Polymerisations under these conditions were very fast, as shown by the considerable warming up of the solutions when the acid phial was crushed. The $\overline{DP}$ of the polymers obtained from the present runs were 100 $\pm$ 5.

16. Interpretation of the polymerisation results.

The evidence collected on the polymerisation of NVC suggests the following conclusions:

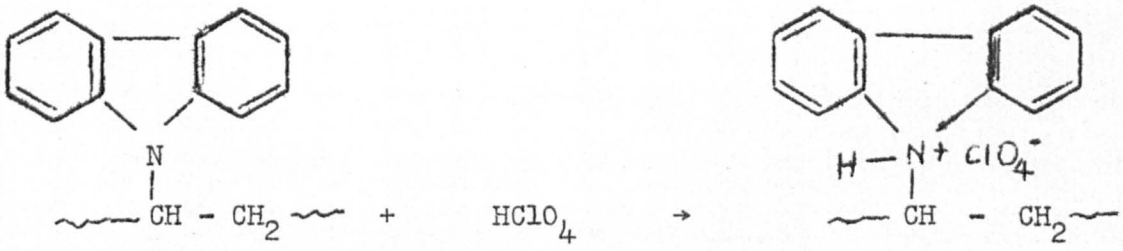
a) As in all the systems studied in this work, a minor bathochromic shift in the absorption maxima occurs when passing from the monomer carbonium ion to the polymer ion; in the case of NVC, for the long wavelength peak, this shift amounts to about 10 mμ (from 746 ± 4 to 755 ± 5).

b) Although carbonium ions are formed under certain conditions, i.e. with high perchloric acid concentration or relatively low monomer concentration, these are certainly not the only species responsible for the polymerisation of NVC in the present system. This is borne out by two important pieces of evidence: first, the fact that if the NVC concentration is sufficiently high, or conversely, if the acid concentration is sufficiently low, no carbonium ion can be detected in the polymerised system (unfortunately, owing to the exceedingly high rate of polymerisation, it was always impossible to record spectra during the polymerisation). Second, quantities of water 4 times as high as the quantity of catalyst, do not poison the system, and the polymerisation proceeds at a rate comparable with that of a "dry" run (see Runs VGP2 and VGP3); the actual concentration of carbonium ions which could be formed and not be seen by spectroscopy is about 1×10^{-6} M or less; this means that in fact in the run with added water, if ions were formed, it would remain

to explain how they could survive in the presence of as much as a 250 fold excess of water.

It seems likely that the second kind of chain carrier is of the same nature as those postulated for the polymerisation of styrene by perchloric acid, and of AN by sulphuric acid, namely ester molecules. This remains to be proved, but the present evidence certainly points in that direction.

c) The species, which is slowly formed after the polymerisation of NVC catalysed by perchloric acid, and which absorbs at 680 mμ and 435 mμ, is most certainly due to the quaternisation of the nitrogen on a monomer unit of the polymer chain, by free perchloric acid. The reaction can be written as follows:



Treatment of diphenylamine with a few drops of 72% perchloric acid produces a green solution, with a spectrum very similar to those obtained in the spectroscopic runs. The quaternisation of this amine would in fact give a salt with a structure closely related to the above reaction product.

Solomon et al[35,36] Chapiro and Hardy[33] and Breitenbach and Snra[32]

have reported that the polymerising solutions containing NVC and various catalysts are yellow or yellow-orange, and attributed this colour to the NVC carbonium ion; the present findings certainly disprove these assertions. In the particular instance of the system NVC - aqueous $HClO_4$ - toluene (and other solvents including acetone and ethyl acetate) recently studied,[36] the postulated carbonium ion mechanism is hardly acceptable, considering the large quantities of water added with the catalyst (which was in some instances introduced into the reaction as a 0.1% aqueous solution). On the contrary, the fact that polymerisation proceeded under those conditions indicates that some other chain carriers must have been responsible for it.

PART IV : A DISCUSSION ON THE RELEVANCE OF THE PRESENT FINDINGS

17. The search for carbonium ions.

I have already mentioned in the Introduction how Whitmore's carbonium ion theory,[34] produced thirty years ago, has since then been the basis for the great majority of the interpretations of the chemistry of reactions taking place in polymerising systems involving acidic catalysts. Whitmore postulated that the interaction of an olefin molecule with an acid molecule HX, would produce a carbonium ion capable of undergoing changes typical of electron-deficient species. In particular, carbonium ions could alternatively react with their anionic counter part to form a covalent molecule (ester), expel a proton with consequent reformation of the olefin, isomerise, or induce the polymerisation of the rest of the olefin present in the reaction mixture. Examples of these and related reactions were given by the author.

About ten years later, following the discovery of co-catalysis in the polymerisation of isobutene catalysed by $TiCl_4$,[38] Whitmore's theory was amplified and became a tool for the interpretation of both acid and Lewis-acid catalysed polymerisations.

The carbonium ion theory has been applied to a great many polymerisation systems since its first formulation; it proved to be a very convenient and equally sound device which never failed its task of providing a mechanistic interpretation for usually rather complicated sets of experimentsl observations.

However, up to the present day, there have been very few attempts to check upon this theory. These are briefly analysed below.

I have already discussed Jordan and Treloar's work on polymerisation systems allegedly involving the formation of the 1-phenyl-ethyl carbonium ion, and the major criticisms to which this work is open (Section 2.2); it was concluded that no direct evidence for the presence of carbonium ions during the polymerisation was in fact offered by these authors.

Recent work performed by Okamura's school[28] has confirmed the doubts expressed about Jordan and Treloar's conclusions; the Japanese authors failed to record any absorption in the visible spectra of 1,2-dichloroethane solutions containing styrene and stannic chloride in concentrations typical or a polymerisation experiment. They noticed however, that when the solvent was saturated with HCl an absorption band at 420 mμ developed when they used the usual concentrations of styrene and $SnCl_4$ (e.g. $[st]_o$ = 0.2 M, $[SnCl_4]$ = 0.03 M). It appeared nevertheless that most probably the first spectrum of the solution was taken when all the monomer had been polymerised (the polymerisation is fast in the presence of HCl), and no conclusions could therefore be drawn from this piece of evidence concerning the nature of the chain carriers. An additional fact, which indicated that the carbonium ions had been formed at the end of the polymerisation was reported by the same authors, viz. that a solution of polystyrene in the same solvent would give rise to a similar absorption band (i.e. at 420 mμ) when stannic chloride and hydrochloric acid were added to it, to give concentrations equal to

those employed for the polymerisation experiments.

An interesting new approach to the problem of the nature of che chain carriers in cationic polymerisation has recently been attempted by Metz.[39] It consisted in following the changes in the dielectric loss at different frequencies occurring in polymerising solutions; the system investigated was styrene - $SnCl_4$ - 1,2-dichloroethane - carbon tetrachloride. The author produced a set of results which allowed him to conclude that ionic species were present during the polymerisation, their concentration remaining constant throughout and after the reaction. Unfortunately, however, one cannot extend these conclusions and assert that the ionic species present were in fact carbonium ions, because the experimental procedure adopted for these runs was far too crude to produce reliable results. The solvent and the monomer were added to the dielectric cell under open conditions; the catalyst phial was crushed in the air, the liquid poured into the cell, and the resulting solution stirred; only at this point was the cell closed. It was thus inevitable that a fairly large amount of moisture was always present in the polymerising solutions, and this prevents any definite conclusions being drawn about the nature of the ions, since it might well be that one or more of the reaction products originating from the interaction of stannic chloride with water were responsible for the high values of the dissipation factor found by the author.

Pepper[40] has in fact shown that the conductivity of stannic chloride solutions in various solvents (including 1,2-dichloroethane)

increases when small quantities of water are added.

The use of dielectric loss measurements to check upon the presence of ions in polymerising solutions is certainly of great interest, and would produce fundamental results if the experiments were carried out under more rigorous conditions; the usual high vacuum manipulation of the reactants would be an essential requirement for any results obtained by this technique to be trustworthy.

The reasons why Pepper and Reilly's[7] alleged evidence for the presence of carbonium ions during the polymerisation of styrene catalysed by perchloric acid cannot be accepted have already been given (Section 3.5.2).

Brown and Mathieson[41] have reported that in the system styrene - trichloroacetic acid - nitromethane the electrical conductivity increases, while the rate of polymerisation decreases when water is added to the reaction mixture. It was concluded that the hydrogen ions formed in the hydration of the acid were not affecting the actual polymerisation either because the protonation of the monomer was not rate determining, or because the acid was consumed by both water and monomer in a competitive reaction. In the light of the present results the second hypothesis seems more likely; if the 1-phenylethyltrichloroacetate is the chain carrier in that system, then relatively large quantities of added water would reduce the ester concentration and thus the rate of polymerisation.

To conclude, the few attempts aiming at verifying Whitmore's theory in polymerisation systems, have all failed and up to the present

work this thirty-years-old theory was still widely used without the support of any irrefutable experimental evidence.

On the other hand there are several examples in the literature of polymerisation systems to which Whitmore's theory can hardly be applied, although this has been done. I have chosen the most striking of these examples to illustrate my point.

Schmitz-Dumont and his collaborators[42] studied the dimerisation of indene and skatole catalysed by strong mineral acids. The reaction medium was a mixture of water and ethanol. In the discussion on the mechanism of dimerisation the authors considered both an ester and a carbonium ion as possible intermediates, but concluded in favour of the second, on the basis of the experimental evidence they had collected. This consisted essentially of kinetic curves illustrating that, irrespective of the acid used, a given kinetic pattern could be exactly reproduced by working at fixed pH. This was taken as proof that the determining factor in the dimerisation reaction was solely the concentration of hydrogen ions, which were in turn responsible for the protonation of the olefin. It is now well known that carbonium ions of the type postulated by these authors cannot be formed in an aqueous-alcoholic medium, and that therefore the dimerisation must have been promoted by some other intermediate.

The other two examples have already been discussed during the course of this Thesis. The first is Pepper and Reilly's carbonium ion interpretation applied to runs with 20 times as much water as

perchloric acid in the polymerisation of styrene. I have shown that much less water is sufficient to prevent the formation of any detectable quantity of carbonium ions after the polymerisation, for this same system (see Section 3.5.3).

The second is the polymerisation of NVC catalysed by aqueous perchloric acid, in different solvents, for which Solomon and co-workers postulated a carbonium ion mechanism; for the reasons discussed above this seems untenable (See Section 16).

All these authors have failed to consider that the carbonium ions they were postulating are very unstable entities, liable to be destroyed even by mildly basic substances. Even the much more stable triphenylmethyl carbonium ion is very sensitive to traces of moisture, and one has to go to very highly conjugated species (such as the tropylium cation, which is stable in ethanol)[43] in order to find more stable carbonium ions. Therefore, unless one is working in a medium of very high acidity (concentrated sulphuric acid, neat hydrogen fluoride, etc.), in which adventitious basic poisons are destroyed before they can attack the carbonium ions, it is wrong to postulate the presence of carbonium ions derived from polymerisable olefins (such as styrene and its derivatives, all the aliphatic olefins, and others), when dealing with systems containing fairly large proportions of water, alcohols and other basic substances. This has been illustrated in many an instance during the course of this work.

18. Pseudocationic and true cationic polymerisations.

The adoption of the term "pseudocationic" is proposed here for polymerisation systems involving an ester, of the kind illustrated on page 112 as chain carriers.

Having discussed the rather discomforting situation in which the chemistry of cationic polymerisation had to stand, a situation characterised by the adoption of a basic common theory which had never been proved irrefutably for any system, and which, moreover, could not be applied soundly to some of these, I will now proceed to discuss the implications of the newly found pseudocationic polymerisations in the light of both the present findings and of some published work which points in the same direction.

As already mentioned (Section 3.5.1) the formation of esters from the interaction of strong acids with olefins, is by no means a new idea. Berthelot,[44] Lwow,[45] Kondakow[46] and Butlerow[47] all postulated the formation of this kind of intermediate to explain the mechanism of olefin polymerisations catalysed by acids. However, these theories lost much of their strength with the advent of the more refined carbonium ion theory; since then only a few authors returned to the old interpretation, with the intent of reviving it by modernisation.

Ipatieff[48] has resorted to an ester intermediate to explain the mechanism of olefin polymerisations catalysed by sulphuric acid. Several years later this author, in an article written in collaboration with Schmerling,[49] pointed to the similarity between the carbonium ion

and ester mechanisms.

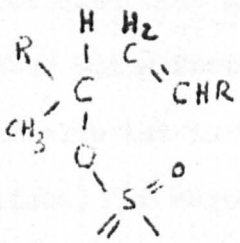
These were, however, rather weak attempts to keep the old theory alive, despite the overwhelming popularity which the carbonium ion interpretation was acquiring.

Wassermann and co-workers[19] have isolated the reaction product of trichloroacetic acid with cyclopentadiene, which is a dimeric ester. The ester was shown to be very reactive and liable to be converted into unsaturated polymers in the presence of more acid. The interpretation of these phenomena was however, entirely based on a carbonium ion mechanism and it was considered that the ester itself could not promote propagation of a chain, and it required the presence of free acid to give active ion pairs.

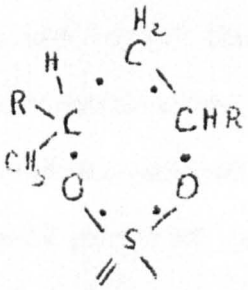
A more serious and radical approach to the problem was attempted in recent years by Fontana.[13,40] His arguments can be summarised as follows:

After having pointed out that no independent physical evidence for the existence of carbonium ion intermediates in the systems for which they have been postulated, has ever appeared in the literature, and that the carbonium ion theory has generally failed to formulate reasonable transition states, Fontana proposed a new theory which would overcome these difficulties. The theory is based upon considerations which find much support in a large number of previously published reaction mechanisms. It consists in considering that the interaction of α-olefins with acid catalysts yields esters which are capable of promoting the polymerisation of the rest of the olefin; the addition of a second olefin molecule to

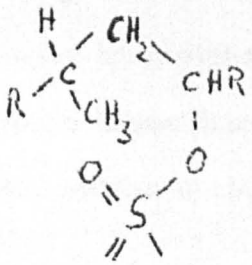
the ester, to form the dimer ester occurs through the formation of a "cyclic transition state with simultaneous displacement of a set of electrons of like spin in a closed circuit about an even number of atomic nuclei". Thus, for sulphuric acid, Fontana writes the following scheme:



Initial State



Transition State



Final State

The author stresses the fact that the ester is not the only species which can be formed in such reactions; depending upon the specific circumstances in which these are carried out, a whole range of possible compounds can form, including associated and dissociated ions.

Finally Fontana discusses how other reactions occurring in the systems considered (such as intramolecular rearrangements) can be explained by his new theory.

At the time of its appearance, Fontana's theory did not receive much attention, for two main reasons:

a) The author's criticisms of the carbonium ion theory went beyond reasonable limits (e.g. the assertion that no transition state had

been formulated for carbonium ion reactions, which is opposed by a fair number of papers dealing with that particular problem).

b) The new theory was just as bad as the old, in so far as it did not provide any direct reference to published experimental work which supported it against that involving carbonium ions. A close examination of the substance which one could extract from Fontana's contribution revealed that after all he did not reject the possibility of carbonium ions being formed under suitable conditions, and the only theoretical novelty lay in the formulation of the six-membered cyclic transition state, for which not even a small piece of experimental evidence could be adduced.

In conclusion, the new idea left the whole matter very much in the same state of urgent need for practical verification; more than new speculative arguments on the nature of the active species in the cationic polymerisation of olefins, one needed new ideas on how to tackle the problem of their direct, experimental identification.

The techniques adopted for the present work provided to a certain degree the answer to this fundamental problem; their principal limitations will be discussed later. For the moment it is profitable to summarise what they have revealed beyond doubt.

The pseudocationic polymerisation of a few monomers promoted by a certain number of catalysts has been studied; in some instances no definite proof could be offered for the existence of an ester acting as chain carrier, in one instance I could reproduce the polymerisation

conditions by substituting for the original catalyst an equivalent amount of the corresponding ester, thus offering direct evidence in support of my interpretation.

On the other hand it was found that carbonium ions are very powerful chain carriers and that when the circumstances allow their formation in the polymerising solutions, a vast increase in the rate of monomer consumption always occurred.

I was also able to show, for more than one system, that the olefin itself is responsible for the stabilisation of the ester formed in the initiation reaction, which is otherwise unstable, and liable to regenerate free acid and subsequently give carbonium ions (Section 3.5.3).

The present study has made the first practical contribution to the search for chain carriers, but the problem still remains very wide. The mode of ester stabilisation by excess of free olefin is obscure, and so is the actual charge distribution in an active ester molecule.

These and similar problems must be studied with one important premise in mind: There are four fundamental parameters controlling the behaviour of systems of the "cationic" type, namely the relative basicity of the olefin to be polymerised, the acidity of the catalyst in the medium chosen, the polarity of the solvent (or its solvation power), and the working temperature.

If one visualises the possible states of the chain carriers as ranging from free ions at one end to unpolarised ester molecules at the other, the actual structure depending upon the working conditions, it will be

clear that in order to shed light on the problems of the nature of chain carriers, a systematic study of the influence of each one of the four variables(holding the other three unchanged) upon the behaviour of the system must be conducted. This will lead to the construction of a four dimensional network, in which more or less definite boundaries separate the zones of pure ionic and pure pseudocationic polymerisations from others in which the presance of both types of chain carriers must be be expected.

The evidence collected in this study constitutes the first step in the construction of such a network.

The influence of the nature of the acid has been studied for the polymerisation of styrene in methylene dichloride at room temperature; under special circumstances,(very high local acid concentrations, or low styrene concentrations) perchloric acid can produce a certain number of carbonium ions, together with the ester 1-phenylethyl perchlorate; these circumstances, however, are rather special and the polymerisation is normally pseudocationic, and catalysed by a number of ester molecules equivalent to the initial quantity of acid added. 1-Phenylethyl sulphate is not a chain carrier under these circumstances, neither is 1-phenylethyl trifluoroacetate, unless a large amount of free trifluoroacetic acid is present to increase the polarity of the medium. When metal halides are used as catalyst the ester molecules produced by the interaction of the catalyst hydrates with styrene are active if "solvated" by an excess of the free halide.

One can conclude that as the anionic moiety of the acid becomes

less basic, the corresponding 1-phenylethyl ester loses progressively its capacity of polymerising the free styrene, probably because the carbon-oxygen bond becomes less polar; the presence of polarising substances in solution, will, however, restore a stronger dipole in the bond and consequently the ester molecule will reacquire its chain-carrier properties. Moreover a large excess of polarising agent will induce a total charge separation in the ester molecule and carbonium ions will be formed (high concentrations of perchloric or sulphuric acid).

The same considerations seem to apply to the effect of changing the monomer for a given catalyst-solvent-temperature situation: An increase in the basicity of the olefin will increase the polarity, and therefore the activity of the ester, and in the extreme case lead to the formation of carbonium ions.

The influence of the polarity of the solvent has not been studied very thoroughly: The use of nitroalkanes did not give the expected behaviour, but it seems likely that the obscure anomalies encountered when working with these solvents are to be attributed to purely chemical, rather than physical, reasons, i.e. to reactions between catalyst and solvents. The results obtained by Pepper and Reilly,[7] indicate that the higher the polarity of the solvent (for chloroalkanes), the faster is the polymerisation, for a given monomer-catalyst-temperature situation; since the polymerisations studied by these authors are in fact pseudocationic, one can conclude that the reasons for the enhancement in the polymerisation rates is probably to be found in the fact that the ester molecule will be

the more polar, (and the rate will be the higher), the more polar the solvent.

The effect of temperature upon the activity of the chain carriers has only been studied for the polymerisation of styrene catalysed by perchloric acid, in methylene dichloride; it is known that a decrease in temperature increases the polarity of methylene dichloride, and I thought that it might be possible to obtain a certain amount of carbonium ions together with the ester, when working at about -90°; this does not happen, however, and the pseudocationic polymerisation of styrene at that temperature proceeds at a very low rate.

Our knowledge of the influence of the four determining parameters upon the nature of the chain carriers is so limited at present, that virtually no prediction can be made seriously about ahy given system, without risking a major disillusion. For the moment the field is in great need of systematic exploration over a large number of widely different systems; the accumulation of this evidence will certainly make the understanding of the chemistry of cationic and of pseudocationic polymerisations more clear and only at that stage will one be able to assess the possible position of a new system in the four dimensional network.

One of the most unpleasant implications of the findings reported in this thesis is that the whole body of published work in the fiel of what was called cationic polymerisation, needs now a drastic revision, as far as the interpretation of the results is concerned. None of the chemical schemes put forward can be accepted before an accurate check on the chemical

species effectively present in the given system has been carried out.

The present findings have shown that carbonium ions are in fact very powerful chain carriers in some instances: The possibility of very low concentrations of these being formed under certain conditions, concentrations too low to be detected by the techniques developed (i.e. below 10^{-6} M), cannot be ruled out, since it is possible, although not very likely, that such small quantities of powerful chain carriers, could still be promoting polymerisation at a reasonable rate.

For a typical anionic polymerisation[51] (k_p = 500 $lm^{-1} sec^{-1}$ for the polymerisation of styrene, with Na^+ as counter ion, in tetrahydrofuran at 25°)[49] the initial rate of polymerisation for $[st]_o$ = 0.2 M and [carbanions] = 10^{-6} M is 6 x 10^{-3} m l^{-1} $min.^{-1}$ As first approximation, one can assume that values of k_p for a true cationic and an anionic polymerisation, performed under similar conditions, are of the same order of magnitude. If carbonium ions were present in the systems studied, at concentrations lower than 10^{-6}M, the rates one would expect on the basis of the above calculation, should be lower than those in fact obtained. This seems to support the conclusion that other chain carriers, namely ester molecules, must be present in these systems.

The kinetic data on a given system will however, help considerably in deciding whether the possibility of small quantities of "unseen" carbonium ions being the chain carriers must be taken into account.

I have been able to find only two references in the literature for polymerisations promoted by ester molecules.

Tokura and Kawahara[52] have recently reported on the polymerisation of styrene in liquid sulphur dioxide catalysed by alkyl and arylalkyl chlorides. At 25°, with $[st]_o$ = 1.32 M and [RCl] = 0.366 M, several chlorides were tested and gave different polymerisation rates. One exception was triphenylmethyl chloride which gave only traces of polymer; benzyl and 1-phenylethyl chloride gave about 15% conversion in two and a half hours, whilst the alkyl chlorides were slightly less active. Hydrochloric acid did not initiate the polymerisation of styrene under these conditions.

It is difficult to conclude, from the evidence published, whether the chain carriers were in fact polarised ester molecules or a small number of carbonium ions originating from partial ionisation of the chlorides, also because no details were given about the experimental procedure.

The second work has been published by Sigwalt and Vairon;[53] these authors polymerised cyclopentadiene in CH_2Cl_2 using Cl_3TiOBu^n as catalyst. The reactions were carried out under vacuum and under anhydrous conditions. The rate of polymerisation were high: at $[catalyst]_o = 2 \times 10^{-3}$ M, $[monomer]_o$ = 0.5 M, the reaction was over in about 20 seconds. The authors showed that the polymerisation was <u>not</u> due to possible traces of $TiCl_4$ present in the catalyst, but did not comment on the mechanism of the reactions involved.

The problem of the mechanism of the different steps involved in a pseudocationic polymerisation still remains to be solved; the scheme of reactions shown on page 112 is a first attempt to represent these. In the scheme the rate determining step is the propagation, with a

six-membered cyclic transition state, which involves the interaction of an ester molecule with a monomer molecule. If this is so, and if analogous situations are postulated for the transfer reactions, the overall process will not differ kinetically from the ionic chain reaction scheme previously formulated by Pepper and Reilly.[7]

PART V : SUGGESTIONS FOR FURTHER WORK

19. Technical aspects.

The spectroscopic device (Chapter One) needs important modifications to allow measurements to be taken at temperatures different from room temperature; the whole of the solution must be kept at the same fixed temperature in order to avoid vacuum distillation of the solvent from one section of the device to another. This can be attained by having the mixing tube vertically mounted above the cell, so that by turning the device up-side down, all the liquid will be collected in the cell.

Another spectroscopic device must be designed for reactions which are too fast, and go to completion before 20 - 30 seconds. This device can be built in such a way that the mixing can take place when the device is already placed in the cell compartment of the spectrophotometer: taps or break seals operated from outside the compartment will be opened while the instrument is already scanning.

20. Chemical aspects.

Of the several problems which this work has revealed, the following seem to me the most urgent:

a) The preparation of esters and the study of their stability, i.e. of their tendency to ionise in different solvents and at different temperatures. The method used to prepare the 1-phenylethyl perchlorate could be applied to other olefins.

b) Among the new olefins to be tested, p-methoxystyrene promises to be one of the most interesting; it is much more basic than styrene and one should find therefore the conditions under which true cationic polymerisation can be attained, especially with perchloric acid.

c) The stability of esters towards water, under polymerising conditions seems to be fairly high, according to the results obtained. A quantitative approach to this problem is however very important: conductivity studies are certainly the most suitable for this.

d) The origin of the transitory pink colour which was observed immediately before the ionisation of the ester in the polymerisation of styrene catalysed by $HClO_4$ (Section 3.1.1), needs to be studied, since it might give some indication of the structure of the ester and of the way in which this generates carbonium ions.

e) The mode of ester stabilisation by excess of styrene can probably be understood by working with olefins incapable of polymerising (because of steric hindrance) but able to interact with perchloric acid to give, depending on the working conditions, an ester or carbonium ions. By removing the problem of the olefin consumption by polymerisation, a study of the ester stabilisation mechanism should become feasible. Compounds like ethyl cinnamate or the polychlorostyrenes seem the most suitable for this study, because their structure is very similar to that of styrene; they cannot polymerise because of steric hindrance.

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